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ON THE IRIDESCENCE OF POTASSIUM CHLORATE CRYSTALS

Part I. Its Spectral Characters

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Received October 27, 1952

1. Introduction

It has long been known that potassium chlorate occasionally crystallises in plate-like forms which display a spectacular iridescence, due to the fact that these crystals are polysynthetic twins and that the light traversing the same is reflected at the composition planes of twinning, thereby giving rise to interference effects. An extensive collection of these iridescent crystals was available to us for investigation, and an opportunity recently arose for making a detailed examination of their optical behaviour. Several surprising and interesting results have emerged from our studies, and it is proposed in the series of papers of which this is the first to describe our findings and discuss their significance.

We may usefully recall here the special features of the iridescence of potassium chlorate which drew the attention of the pioneer workers in the field and led them to the explanation stated above. When the crystals are viewed normally, the coloured reflections are absent; they develop and increase in intensity with increasing obliquity of observation, the colour changing more or less rapidly at the same time. Individual cases differ greatly in respect of the brilliancy and colour of the iridescence which they display and in respect of the sequence of changes noticed with increasing angle of incidence of the light. In all cases, however, and irrespective of such angle of incidence the coloured reflection vanishes completely for particular azimuths of the plane of incidence, disappearing twice in each complete revolution as the crystal tablet is rotated in its own plane. A specially noteworthy feature is that the coloured reflection when examined through a spectroscope appears in many cases as a narrow monochromatic band or else as a number of such bands. These bands shift towards shorter wavelengths in the spectrum and simultaneously broaden out to a notable extent as the angle of incidence is increased. The light transmitted by the crystal exhibits effects complementary to those observed by reflected light.

2. SPECTRAL CHARACTERS OF THE IRIDESCENCE

It appeared to us important to obtain a series of spectrograms with selected crystals exhibiting the character of the reflected and of the transmitted light in varying circumstances of observation, *viz.*, over a wide range of angles of incidence, extending from nearly zero upwards, as also over a range of azimuths of incidence extending from that at which the reflections vanish to that at which they attain maximum intensity. One may expect on theoretical grounds to find an increase in the spectral width of the bands of reflection when the azimuthal angle measured from the former position increases from zero to 90°, the angle of incidence of the light remaining the same. This effect has actually been observed by us. Surprisingly enough, however, other and even more striking changes in the nature of the spectra are noticed when the azimuthal angle is changed without changing the angle of incidence.

The spectrograms reproduced in the Plates accompanying this paper were obtained with five crystals selected for the reason that all of them at nearly normal incidence of the light exhibit a monochromatic reflection in the visible region of the spectrum. The source of light used was a metal filament lamp run with a heavy current and the spectrograms were recorded with Hilger glass instruments. The crystals were mounted in Canada balsam between two thin prisms of glass facing opposite ways, thereby eliminating the usual reflection from the external faces. We shall refer to the five crystals as A, B, C, D and E respectively. At nearly normal incidence they exhibit respectively deep red, indigo blue, orange red, greenish yellow and green iridescence.

Crystal A.—At nearly normal incidence, this has a reflection maximum in the visible spectrum at about λ 6500 in the red having a total width of 100 A.U. In the ultra-violet it shows a reflection maximum at about λ 3290 having a width of about 20 A.U., thereby making it evident that the band in the red corresponds to a first-order reflection. Fig. 1 in Plate IV shows a series of spectrograms of the light in the visible region reflected by this crystal; the plane of incidence was that of maximum intensity of reflection and the seven successive spectrograms show the effect of increasing the angle of incidence by steps from about 5° to 55°; the exposure times were adjusted suitably so that all the spectra were satisfactorily recorded on the same plate. Fig. 2 in Plate IV reproduces a similar series of spectrograms, the azimuth of incidence being however kept constant and nearly that at which the reflections vanish. Longer exposures had naturally to be given for Fig. 2 than for Fig. 1.

Examining these spectra, a striking feature is that the principal reflection maximum is accompanied by an extended trail of subsidiary maxima of relatively feeble intensity. The distribution of intensity of these subsidiary maxima shows a notable asymmetry about the principal maximum. They are both more numerous and more intense on the side of longer wave-lengths; on the side of shorter wave-lengths, the intensity falls off rapidly to zero.

A comparison of Figs. 1 and 2 in the Plate clearly shows that in both cases, the width of the principal maximum increases with increasing obliquity of incidence. On the other hand, it is clear that such increase is definitely less in Fig. 2 where the azimuthal angle is small instead of being 90° as in Fig. 1. To illustrate this further, a series of spectrograms have been recorded keeping the angle of incidence nearly constant at about 55° and varying the azimuthal angle by successive steps from nearly 0° to 90°. This series is reproduced as Fig. 1 in Plate VIII and exhibits a notable increase of the width of the principal maximum in the series. On the other hand, the subsidiary maxima do not exhibit any such widening. Likewise, in the two series of spectrograms taken with increasing obliquity and at a constant azimuth there is no obvious increase in the width of the subsidiary maxima. The increasing dispersion of the instrument in the region of shorter wave-lengths results, however, in a corresponding progressive alteration in their apparent width.

3. Splitting of the Reflection Maxima

We now turn to the spectrograms reproduced in Plates V, VI and VII which were recorded with crystals B, C and D respectively on the same general plan as those of crystal A reproduced in Plate IV. Before referring to the features appearing in these spectra, some particulars should be mentioned concerning these crystals. Crystal B gives at nearly normal incidence a reflection maximum at about λ 4780 and 20 A.U. wide; another reflection maximum appears at about λ 3225 with a spectral width of only 8 A.U., from which it is clear that the band in the visible corresponds to a second-order reflection. Crystal C gives at nearly normal incidence a reflection maximum at λ 6150 about 40 A.U. wide. In the violet region, a second maximum at about λ 4155 with a width of 12 A.U. is observed. These two evidently correspond to the second and third order reflections respectively. Crystal D gives a principal maximum at λ 5350 about 20 A.U. wide. This is probably a first-order reflection.

As in the case of crystal A, two series of spectrograms were recorded with each of the crystals B, C and D; in the first series the azimuthal angle was 90° while in the second series it was nearly zero. In each series the

angle of incidence was altered by steps from 5° to 55°. A comparison o Figs. 1 and 2 in the Plates referring to each of these crystals shows a striking difference in the nature of the spectra in the two series. When the azimuthal angle is small, the principal maximum of reflection splits symmetrically into components which drift away from each other and also towards shorter wavelengths with increasing angles of incidence. On the other hand, in the spectra recorded at an azimuthal angle of 90° the principal maximum of intensity does not split but merely widens out and drifts towards shorter wavelengths. Simultaneously, however, an additional component or " ghost " appears on either side of the principal maximum in the spectrum but well removed from it. These ghosts or companions broaden and become more intense with increasing obliquity of incidence and the entire triplet simultaneously drifts towards shorter wavelengths. The widening of the central maximum of the triplet in one series of spectra is of the same order of magnitude as the separation of the two components of the doublet in the second series. While this general description covers the effects observed with three crystals, there are some differences in detail. to which attention may be drawn.

Crystal B.—As in the case of crystal A, a trail of subsidiary bands accompanies the principal maximum of reflection. These are most clearly seen in the series of spectra reproduced as Fig. 1 in Plate V. One notices that the bands are very fine and numerous. However, they exhibit periodic variations of intensity which convey the impression that a second set of broad bands are superposed thereon.

In order to exhibit the change-over in the nature of the spectra in passing from the azimuthal angle 0° to 90°, a third series of five spectrograms were recorded in which the obliquity of incidence was kept nearly constant at about 45° and the azimuthal angle altered by steps. These are reproduced as Fig. 2 of Plate VIII from an inspection of which it will be seen that the two components of the reflection maximum in the doublet series coalesce together so as to form the broad central band in the triplet series, while simultaneously, the outer components of the triplet appear and increase in width and intensity.

Crystal C.—As will be seen on a comparison of the figures in Plates V and VI, the general features of the principal reflection maxima exhibited by crystals B and C are similar; the components for crystal C appear rather closer together than for crystal B. It is of interest to note that the doublets and triplets into which the maxima split are to be observed also in the third order reflection appearing towards the violet end of the spectrum. The subsidiary maxima in the spectra of crystal C are somewhat closer than in

the case of crystal A but much farther apart than those of crystal B. Their distribution in intensity is very regular and does not show the peculiar features observed in the last-mentioned case.

Crystal D.—The components of the triplet are not single but exhibit much detail. It is noteworthy that the components of the reflection maximum in the doublet spectra likewise exhibit a structure. Indeed at oblique incidences, we actually notice in Fig. 2 of Plate VII that the reflection maximum has split into four broad components instead of two as in the case of crystals B and C. The subsidiary maxima in the spectra of this crystal are sharp and numerous, and do not exhibit the regularity of spacing noticed in the case of the other crystals.

4. Transmission Spectra

As is to be expected, the transmission spectra in all cases are complementary to the reflection spectra. When the azimuthal angle is nearly zero the reflections and hence also the extinctions are very weak, and only the strongest of the latter are recorded, if at all, in transmission. More detail is however observable in the transmission spectra corresponding to the azimuths of incidence at which the reflection has a maximum intensity.

Figs. 1 and 2 in Plate IX and Figs. 1 and 2 in Plate X are a series of transmission spectra recorded with crystals A, B, C and D respectively at an azimuthal angle of 90°, and at varying obliquities of incidence. It will be seen on a comparison with the figures in Plates IV to VII that they reproduce only the strongest features in the corresponding reflection spectra. In particular, the triplets of the principal maxima exhibited by crystals B, C and D are also to be seen in transmission.

On account of their extreme weakness, the subsidiary maxima are scarcely to be seen in the transmission spectra. Figs. 1 and 2 in Plate XI however show for comparison the reflection and transmission spectra of crystal E at varying angles of incidence and at an azimuthal angle of 90°. This crystal shows at nearly normal incidence a maximum of reflection at about λ 5350 and about 150 A.U. wide, and this widens and drifts towards the violet at increasing angles of incidence. The close correspondence in the positions and intensities of the subsidiary maxima of reflection and extinction can be clearly made out from the figures. Fig. 3 in Plate XI shows the enormous increase in the intensity of the reflections given by this crystal with increasing azimuthal angle. It will be noticed however, that the positions of the subsidiary maxima remain practically unaltered. Studies made with this particular crystal at very oblique incidences show that both in reflection and extinction, there is a notable widening of the principal band as the azimuthal angle is increased from 0° to 90°.

5. DISCUSSION OF THE RESULTS

Studies described more fully in the second paper of this series have shown that the components of the doublet and the outer components of the triplet recorded with crystals B, C and D are strongly polarised, and related effects have also been observed with crystal A. A detailed discussion of the experimental facts reported in the present paper has therefore to be deferred till we have described and discussed the polarisation effects. The appearance of subsidiary maxima accompanying the strong monochromatic reflections is however intelligible in the light of the general theory of the optical behaviour of stratified media. Reference may be made in this connection to two recent papers in these *Proceedings* by G. N. Ramachandran dealing with the spectral character of the reflection of light from stratified media and the analogous theory of X-ray reflections in crystals. The spectrograms reproduced in the present paper recall in a striking manner the theoretical curves for the spectral distribution of intensity appearing in the first of the two papers by Ramachandran, quoted above. As has been stressed by him, the spectral width of the principal reflection maximum for a regularly stratified medium is determined by the absolute reflecting power of a single stratification and not by the total number of stratifications present, if the latter be large enough. The experimental findings regarding the effect of varying the azimuth of incidence brought to notice in the present paper fall into line with this indication of the theory.

6. SUMMARY

Spectrograms obtained with five iridescent crystals of potassium chlorate at varying azimuths and obliquities of incidence have been obtained and are reproduced with the paper. Some of the results observed are explicable in terms of the general theory of the optical behaviour of a regularly stratified medium, *viz.*, (*a*) the appearance of a whole series of subsidiary bands accompanying the principal maxima and distributed asymmetrically about them and (*b*) the variation of the spectral width of the principal maximum with change of azimuthal angle and obliquity of incidence. Other striking effects are however also observed which are not so explicable, *viz.*, when the azimuthal angle is nearly zero, the principal band splits into a doublet the components of which drift apart progressively and also shift towards shorter wavelengths with increasing obliquity of incidence. When the azimuthal angle is 90° the crystals exhibit the principal maximum as a triplet, the central component of which has a width of the same order of magnitude as the separation of the doublet in the preceding case, while its outer components are much further apart.

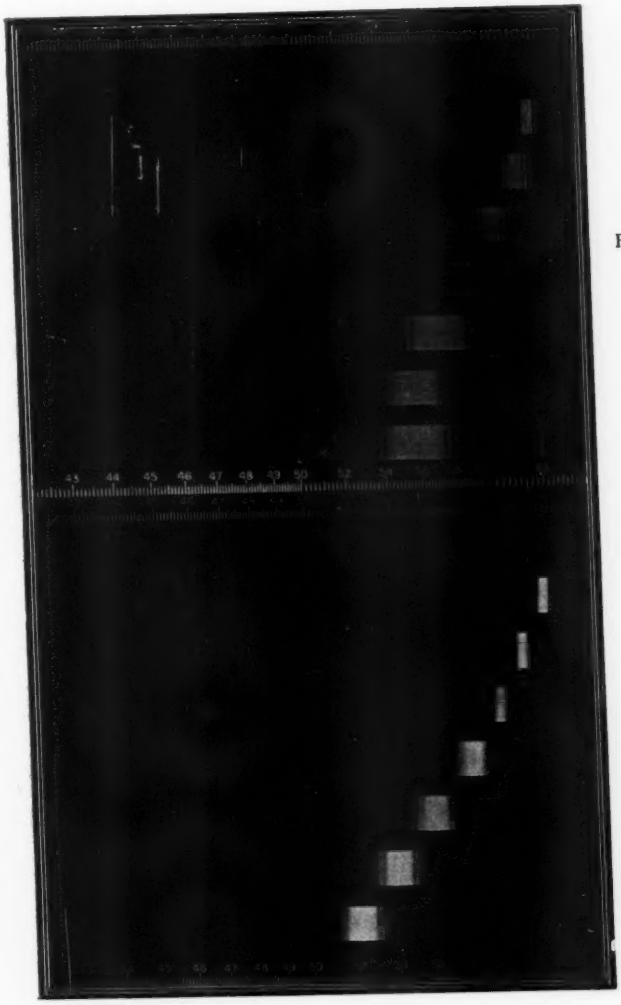


FIG. 1

FIG. 2

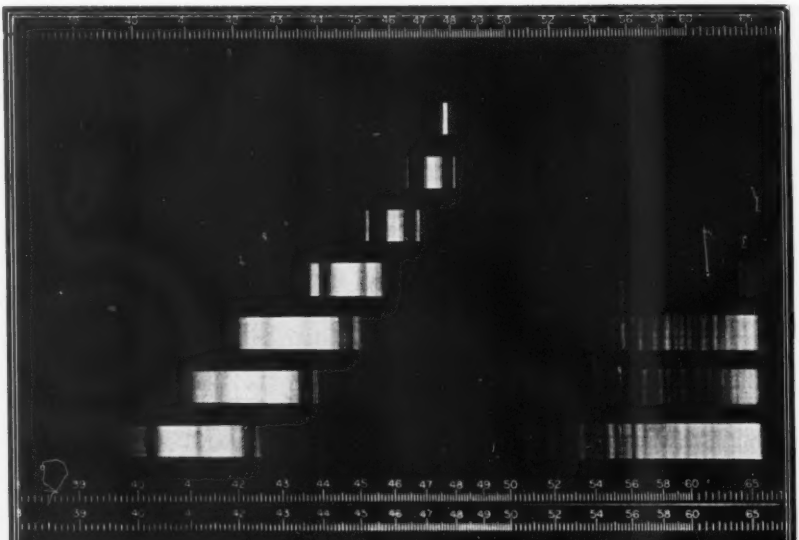
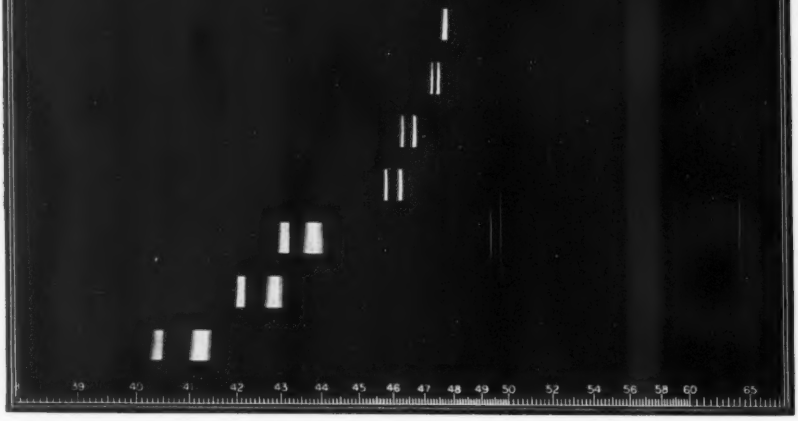


FIG. 1



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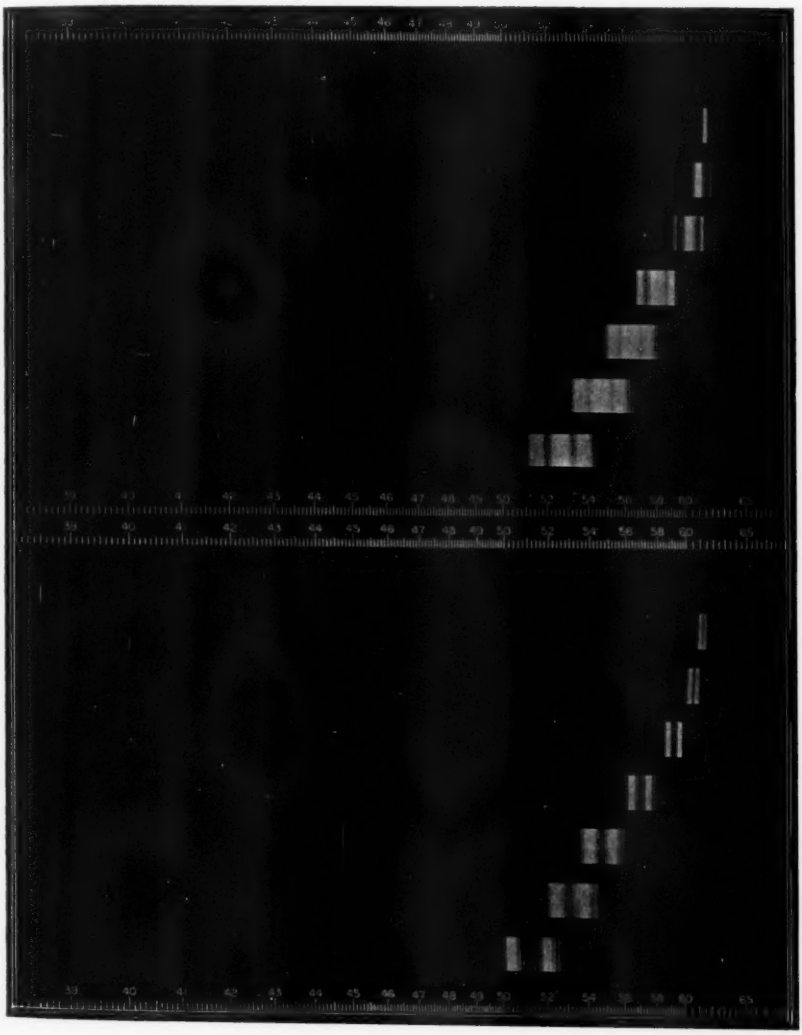

FIG. 1

FIG. 2

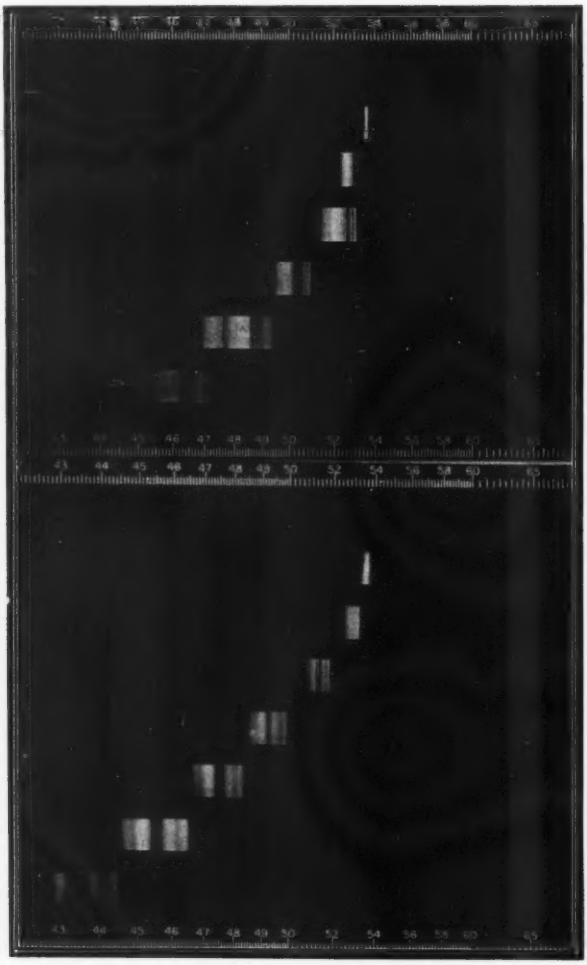

FIG. 1

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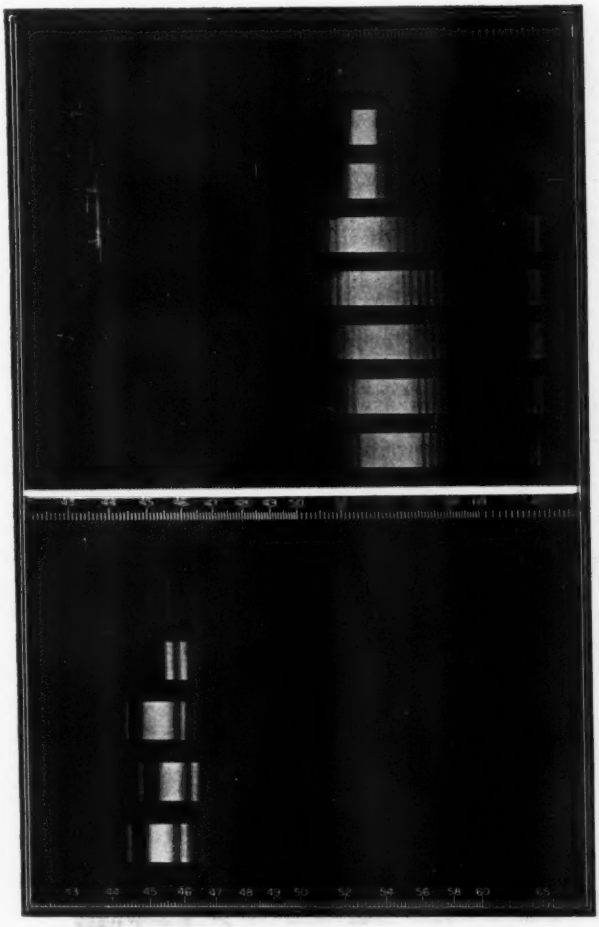

FIG. 1

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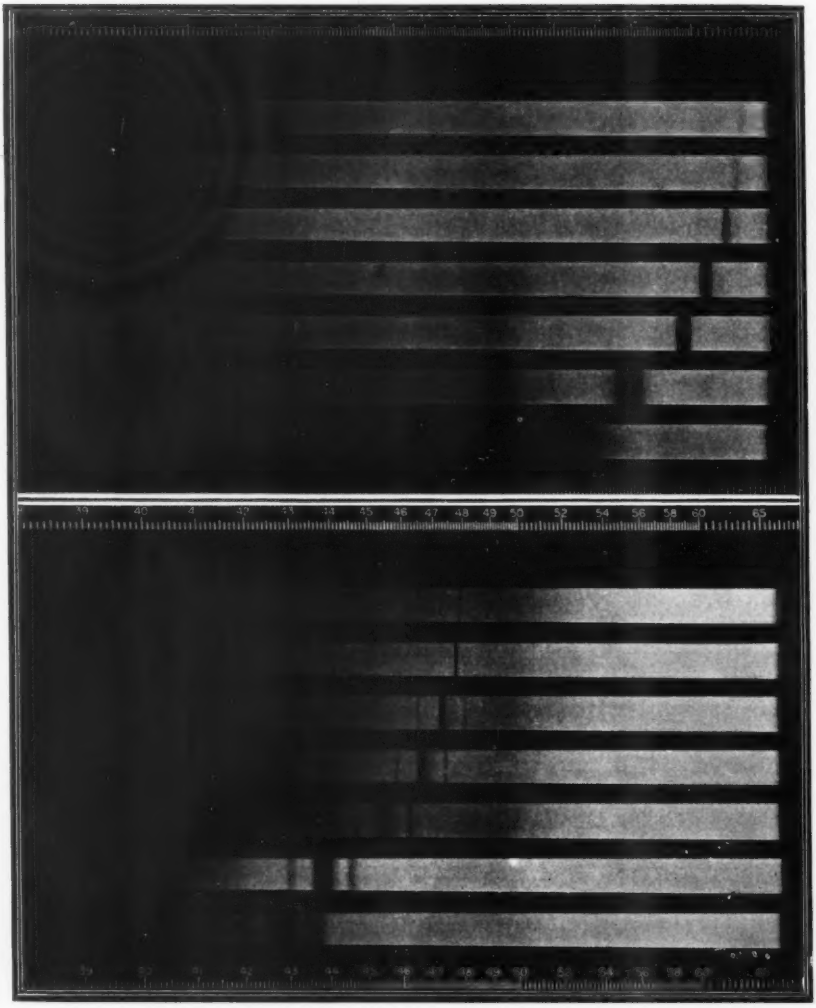

FIG. 1

FIG. 2

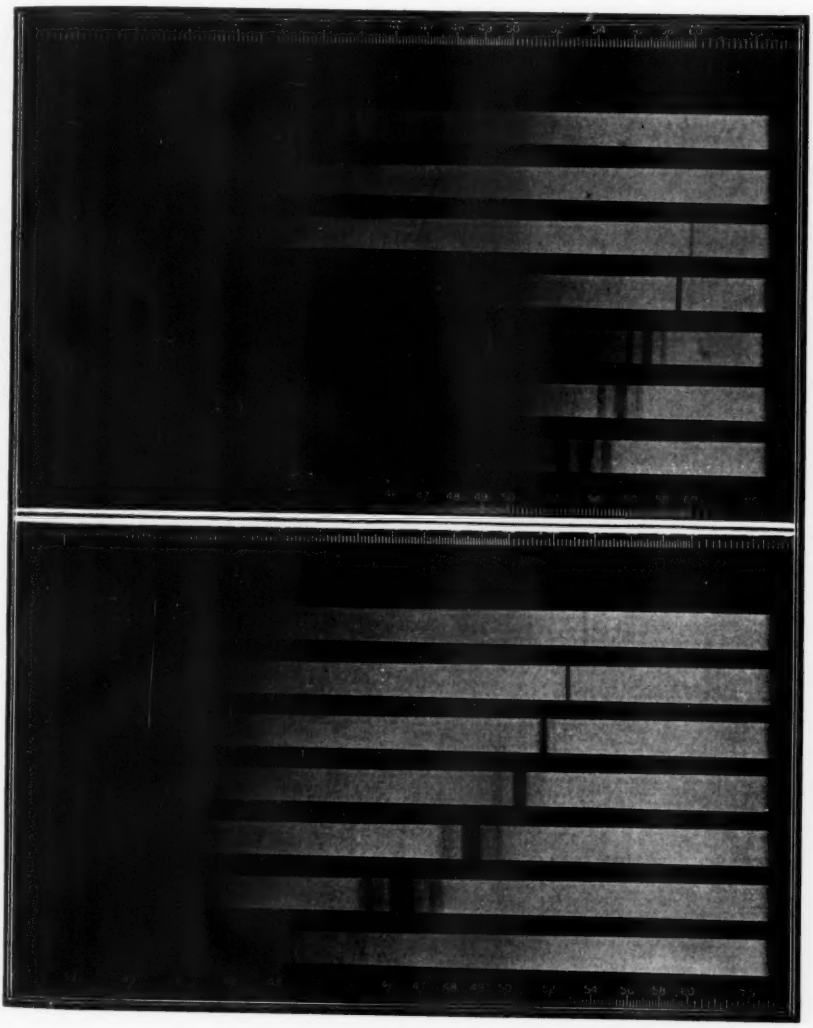

FIG. 1

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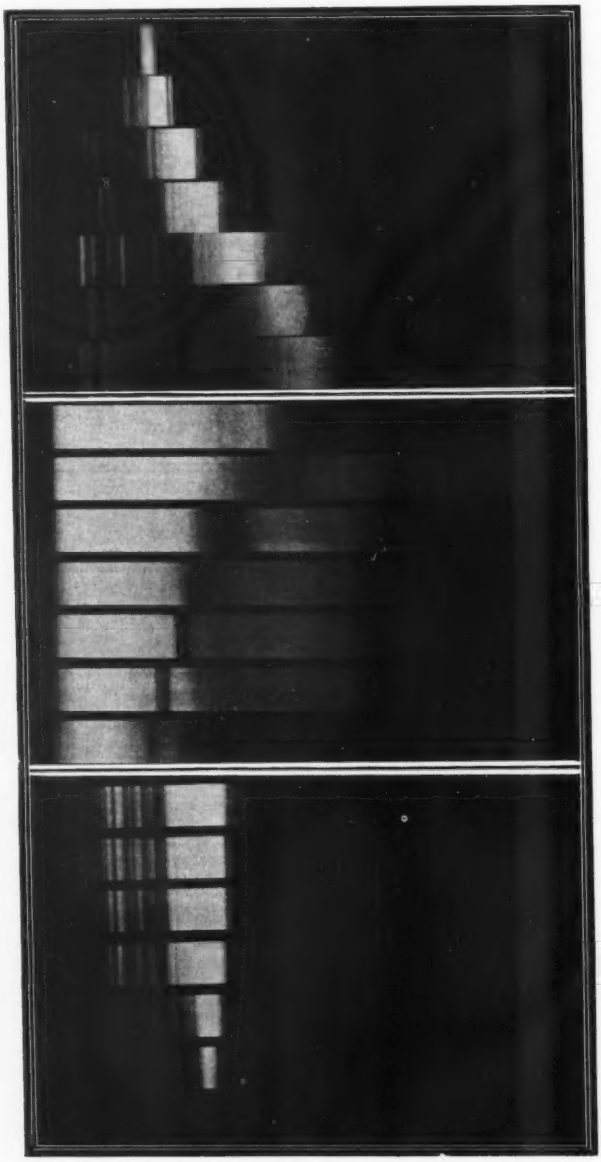

FIG. 1

FIG. 2

FIG. 3

ON THE IRIDESCENCE OF POTASSIUM CHLORATE CRYSTALS

Part II. Polarisation Effects

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Received October 29, 1952

1. Introduction

A remarkable fact about the iridescence of potassium chlorate is that examples are frequently forthcoming in which the reflections are monochromatic, indicating a high degree of regularity of the stratifications as well as the presence of a great number of them. As we have seen in the preceding paper, an examination of the reflection spectra of such crystals reveals features that are in accord with the general theory of the optical behaviour of a regularly stratified isotropic medium. Nevertheless, it is not to be supposed that such a theory would suffice to explain all that is actually observed in the present case. Indeed the iridescence is itself a consequence of the birefringence of the medium coupled with the fact that the alternate layers of it are differently orientated. It follows that a proper theory has necessarily to be based upon a consideration of the propagation of light through a birefringent medium and of the specific characters of a reflection at a twin plane boundary.

2. Crystal Form and Birefringence

Potassium chlorate crystallises in the holohedral class of the monoclinic system; in other words the crystal has both a two-fold rotation axis and a plane of symmetry perpendicular to it. An examination of the tablet-shaped iridescent crystals in convergent polarised light readily enables one to convince oneself that the two-fold rotation axis and the plane of symmetry are oriented alike for all the components of the twinned crystal and that the former is parallel to the external faces of the tablet and that the latter is perpendicular to it. When the tablet is viewed normally between crossed polaroids and rotated in its own plane, two positions of extinction are obtained; in both these positions, when an extended source of light is viewed through the combination, a dark straight isogyre is seen crossing the field from end to end. It follows that the plane of observation marked out by this isogyre contains two of the principal optical vibration directions, while

the third is perpendicular to it. In other words, the symmetry plane containing two of the principal vibration directions is normal to the face of the tablet, while the other principal vibration direction coinciding with the two-fold rotation axis lies in that face. Observations made with rhombus-shaped tablets show that the two-fold axis bisects the acute angle of the profile, while the symmetry plane bisects the obtuse angle in it.

The detailed discussion of the theory of twin-plane reflection given by Rayleigh in his pioneer investigation on the subject is based on the assumption that the crystal is feebly birefringent. This however is far from being actually the case for potassium chlorate. The three principal refractive indices of the crystal for sodium yellow light, are given in the literature as 1·5241, 1·5174 and 1·4099, and the crystal is thus strongly birefringent. On the other hand, one would not be far wrong in describing the substance as a close approximation to a uniaxial crystal in its optical behaviour. The angle between the two directions of single wave-velocity is given in the literature as 27° for sodium yellow light.

3. THE VANISHING OF THE REFLECTION IN THE SYMMETRY PLANE

Very simple considerations indicate that the reflection at the twin-plane boundaries should vanish—as is actually the case—when the plane of incidence coincides with the plane of symmetry.

The location of the principal optic directions in the symmetry plane is shown in Fig. 1, OX and OY referring to the upper side and OX′ and OY′ to the lower side of a twinning plane. The third vibration direction OZ is perpendicular to the plane of the paper. Since the upper and lower halves of the diagram are mirror images of each other, it follows that the coefficient of reflection at the boundary for any given angle of incidence would be the same whether the incidence is from above or from below. On the other hand, it follows as a consequence of the principle of reversibility that the reflection coefficients should be of opposite sign according as the wave is incident on one side or the other of the boundary. As these two results are inconsistent, it follows that the reflection coefficient should vanish for all angles of incidence and all states of polarisation of the incident light, in the case under consideration.

4. THE POLARISATION OF THE REFLECTION BY A TWIN PLANE

The foregoing result may be interpreted physically in terms of the polarisation of the medium produced by the field of the light wave traversing it. If the vibration be perpendicular to the plane of symmetry, the polarisation is obviously the same on both sides of the boundary; there being no

discontinuity, there is no reflection. The same situation subsists when the direction of vibration is in the symmetry plane and the incidence is normal. For oblique incidences, the polarisation does indeed exhibit a discontinuity at the boundary, but this lacks a component transverse to the direction of travel of a reflected wave and hence there is no reflection.

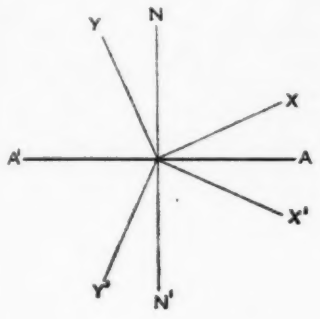


FIG. 1

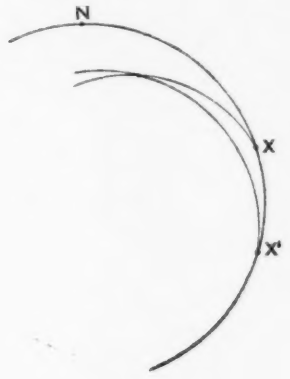


FIG. 2

The foregoing considerations assist us to derive in a very simple manner the characters of the reflection at the composition plane of twinning when the direction of travel of the incident light-waves in the medium does not lie in the symmetry plane but makes a small angle with it. The latter condition allows the azimuths and obliquities of incidence to be varied subject only to the restriction that if the azimuthal angle is large, the angle of incidence should be small. In all such cases, the reflection would necessarily be weak and the incident and transmitted waves would therefore differ but little in amplitude. The corresponding directions of vibration would however be different on the two sides of the boundary, and the reflection occurring at the latter would be the result of a sudden change in the direction of the polarisation at the boundary and not of a discontinuity in its magnitude.

In Fig. 2, the normal to the boundary and the principal vibration directions OX and OX′ on either side of it are shown as points N, X, X′ on a great circle. Two other great circles have been drawn through X and X′ containing respectively the directions of travel of the incident and transmitted waves. These circles cut each other at a small angle and the possible directions of vibration may be assumed to be either parallel or perpendicular to them, since the optical behaviour of potassium chlorate closely approximates to that of a uniaxial crystal with OX or OX′ as the optic axis. The

vector difference in the polarisation on the two sides of the boundary which results in a reflection is transverse to the mean direction of the polarisations due to the incident and transmitted waves. Hence, we deduce that if an ordinary wave is incident on the twin-plane boundary, it is reflected as an extraordinary wave and *vice versa*.

The validity of the result stated above is restricted to the cases considered in which the twin-plane reflection is weak in comparison with the incident and transmitted waves. More generally, a discontinuity in magnitude as well as in direction of the polarisation at the boundary would have to be considered. There would then be both an ordinary and an extraordinary reflected wave and not merely one or the other. If, for example, the plane of incidence is perpendicular to the symmetry plane, only in the particular case of nearly normal incidence of the light, and not at all incidences, could we expect the special law of polarisation stated above to be valid.

5. The Case of Nearly Normal Incidence

As already remarked, potassium chlorate is strongly birefringent and the refractive indices for waves incident nearly normally are very different for the two possible directions of vibration, namely, 1·52 and 1·47. In these circumstances it is distinctly surprising that the crystals give at such incidences, a single sharply defined monochromatic reflection or a series of such reflections. The reason for this is to be found in the special law of polarisation shown above to be valid for such incidences. Considering a pencil of light incident on the crystal, it divides into two beams travelling with very different velocities, the ordinary ray with the lower velocity and the extraordinary ray with the higher velocity. However, the ordinary ray is reflected at the successive twin boundaries and travels backwards as an extraordinary ray with the higher velocity, while similarly the extraordinary ray is reflected and travels back as an ordinary ray with a lower velocity. Hence the total light path is to a very close approximation the same in both cases, and we observe sharply defined monochromatic bands in the spectrum of the reflected light which give no indication that the stratifications giving rise to them are of a strongly birefringent material.

6. Explanation of the Triplet Bands

The situation stated above is radically altered when the light is incident obliquely in a plane perpendicular to the symmetry plane. For, in this case, an ordinary wave travelling downwards is reflected back both as an ordinary wave and as an extraordinary wave, while similarly the extraordinary wave is reflected back both as an ordinary wave and as an extraordinary wave. Hence we have four distinct trains of reflected waves, the light paths traversed

by the first two of which are so widely different that we can expect them to manifest themselves independently in the spectrum of the reflected light, *viz.*, (i) incident and reflected as ordinary waves, (ii) incident and reflected as extraordinary waves, and (iii) and (iv) incident as ordinary and reflected as extraordinary waves or *vice versa*. For the reasons stated above, the first and the second groups may be expected to appear as monochromatic reflections well removed from each other on either side of a central group comprised of the third and fourth set of reflections. These outer components would be of vanishingly small intensities when the incidence is nearly normal, but would gain in this respect as the incidence is made more oblique. The third and fourth groups would by reason of the geometric symmetry, have identical optical paths and would therefore not be spectroscopically separable.

7. Explanation of the Doublet Bands

The case in which light is incident obliquely in an azimuth nearly coinciding with the symmetry plane may now be considered. Here, as we have seen, an ordinary wave is reflected only as an extraordinary wave and *vice versa*. The light paths however lie on opposite sides of the normal to the face of the crystal. Hence, unless the alternate components of twinning are all of equal thickness, the total light path of a wave entering as an ordinary and reflected back as an extraordinary wave would not be the same as that of a wave entering as an extraordinary and reflected back as an ordinary wave. In these circumstances, the wavelengths for which the reflections reinforce each other would not be the same in the two cases, and the monochromatic reflection observed at nearly normal incidences would split into a doublet, and the doublet separation would increase progressively with increasing obliquity of incidence. As the reflections are weak, the components of the doublet may be expected to be fairly sharply defined. A further remark may be made. Since the appearance of the doublet is a consequence of the optical paths on the two sides of the normal being different, a rotation of the crystal through 180° about the normal should result in a reversal of the situation; the extraordinary and the ordinary reflections would interchange their positions in the spectral doublet when the crystal is rotated through 180°.

8. Some Observational Facts

We now return to the theoretical result deduced in Section 4 above, *viz.*, that in certain circumstances an ordinary wave incident at a twin plane boundary is reflected as an extraordinary wave and *vice versa*. An observational test of this may be readily made. A bright source of light is viewed by reflection in the crystal set at such an azimuth that the coloured reflection vanishes and the setting is then altered a little so that it reappears. It is then

found that if the incident light be unpolarised, the reflected light is also unpolarised, indicating that the reflection coefficients are equal for the ordinary and the extraordinary waves. If however the incident light is plane-polarised in such manner that only either the ordinary ray or the extraordinary ray traverses the crystal, the coloured reflection is also plane-polarised but in a reciprocal fashion; it is quenched if the polariser and analyser are set in parallel positions, but comes through if they are crossed.

As is well known, a strongly birefringent crystal transforms a beam of plane-polarised light traversing it into elliptically polarised light which would not be quenched by an analyser set in any position. In the particular case under consideration, however, this difficulty does not arise, since the plane of incidence is nearly coincident with the symmetry plane of the crystal which contains two of the optical vibration directions while the third is perpendicular to it; the ellipticity introduced in these circumstances is therefore negligible. Its disturbing effect can however be made evident by setting the polariser so that the vibration direction is neither parallel nor perpendicular to the plane of incidence. It is then found that the reflection cannot be quenched at any setting of the analyser.

The foregoing considerations suggest that for a complete study of the laws of twin-plane reflection at all azimuths of incidence, it is necessary to use very thin plates in which the iridescent layer is not overlaid by untwinned material. Observations made with such crystals further confirm the theoretical results deduced in Section 4 above and show that in the particular case when light is incident in a plane perpendicular to the symmetry plane, the special law of polarisation is only valid if the incidence of light on the crystal is nearly normal. The observations suggest that at more oblique incidences the vibration in the reflected light is neither parallel nor perpendicular to that in the incident waves. Such a result becomes readily intelligible when it is recalled that at such incidences the reflected light includes both an ordinary and an extraordinary component and not merely one or the other (*vide* Section 6 above).

In his theoretical paper on the reflection of light at a twin-plane in a crystal, Rayleigh showed that when the plane of incidence is perpendicular to the plane of symmetry, the polarisation of the reflected ray would be reversed in the act of reflection; in other words if the incident light is polarised in the plane of incidence, the reflected light would be polarised in the perpendicular plane and *vice versa*. The theoretical derivation was based on the assumption that the birefringence of the crystal is very weak. This assumption is however not in agreement with the facts for the case of

potassium chlorate. It is therefore not surprising that Rayleigh was unable to confirm the theoretical prediction by observations except in the particular case of nearly normal incidence.

9. Polarisation of the Spectral Components

The remarks in the foregoing section refer to the behaviour of the reflected light when examined without the aid of spectral analysis. We shall now pass on to consider the very interesting polarisation effects exhibited by the spectral components of the reflected light in various cases. The facts of observation will be succinctly described and the reader will have no difficulty in verifying that they afford a striking confirmation of the origin of the spectral components given earlier in this paper. It should be understood that the circumstances of observation are invariably those described in the second paragraph of Section 4. When reference is made to a polariser or an analyser, it is to be understood that their vibration directions are set such that they are either parallel or perpendicular to the plane of incidence as the case may be.

The Case of Nearly Normal Incidence.—The unresolved maximum in the spectrum of reflected light is unpolarised if the incident light is unpolarised. If the incident light is polarised, the unresolved maximum is polarised in the *reverse* fashion and is therefore extinguished by an analyser set *parallel* to the polariser.

The Triplet Bands.—The outer components of the triplet described in Section 6, when observed with incident unpolarised light, are found to be plane-polarised in two mutually perpendicular directions. One or the other component is extinguished when viewed through an analyser appropriately set. If the incident light is polarised in one or another of two perpendicular directions, one or the other of the two components is found to be extinguished. The surviving outer component is also extinguished if viewed through an analyser in the *crossed* position. The central band of the triplet behaves in a fashion similar to the unresolved maximum referred to above in the case of normal incidence.

The Doublet Bands.—With incident unpolarised light, the components of the doublet described in Section 7 are plane-polarised in mutually perpendicular directions. In this case, if the crystal be turned round through 180°, the planes of polarisation of the two components are interchanged. With incident polarised light, one or the other component is extinguished. The surviving component is also extinguished if the analyser is set *parallel* to the polariser.

10. DESCRIPTION OF THE PLATES

The spectra reproduced in Plates XII and XIII illustrate the polarisation effects briefly described above. They were obtained with the crystals designated as A, B, C and D in Part I of the present series of papers and whose spectra were illustrated in the plates accompanying that paper. For convenience of reference the crystal used and the setting in which it was placed have been entered at the head of each vertical column in Plates XII and XIII. In setting I, the plane of incidence was normal to the plane of symmetry and the angle of incidence was small. In setting II, the plane of incidence was nearly coincident with the plane of symmetry and the angle of incidence was large. P entered in the horizontal row of the figure denotes that the incident light was polarised, but that no analyser was employed, while A denotes that the incident light was unpolarised while the reflected light was analysed. If both P and A are entered, it signifies that incident light was polarised and that the reflected light was analysed. The angle which the direction of vibrations of the polariser and the analyser respectively, make with the plane of incidence have been entered after the letters P and A.

The following special remarks may be made.

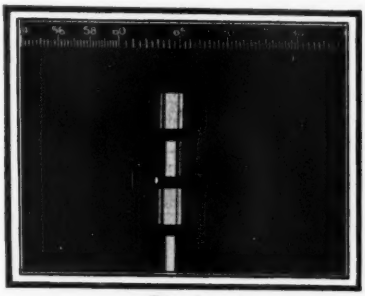
Figure A I.—The pictures of this crystal with polariser or analyser alone have not been reproduced as they were all similar to each other. The picture appearing in Plate XII was taken with both polariser and analyser. Notice that the reflection is weak when the polariser and analyser are parallel and strong when they are crossed.

Figure A II.—Note the change in spectral width and the spectral shift of the reflection with the change in position of the vibration direction of the polariser or the analyser alone. Note also that the reflection vanishes when the polariser and analyser are parallel and that it appears when they are crossed.

Figure B I.—Note the plane polarisation of the outer components of the triplet and the fact that they almost disappear when the polariser and analyser are crossed and that one or the other of the outer components reappears strongly when they are parallel. The central band becomes very weak when they are parallel, whereas it comes out strongly when they are crossed.

Figure B II.—Note the nearly perfect polarisation of the components of the doublet and that one or the other appears when polariser and analyser are crossed whereas both of them disappear when they are parallel.

A I



P0 A90

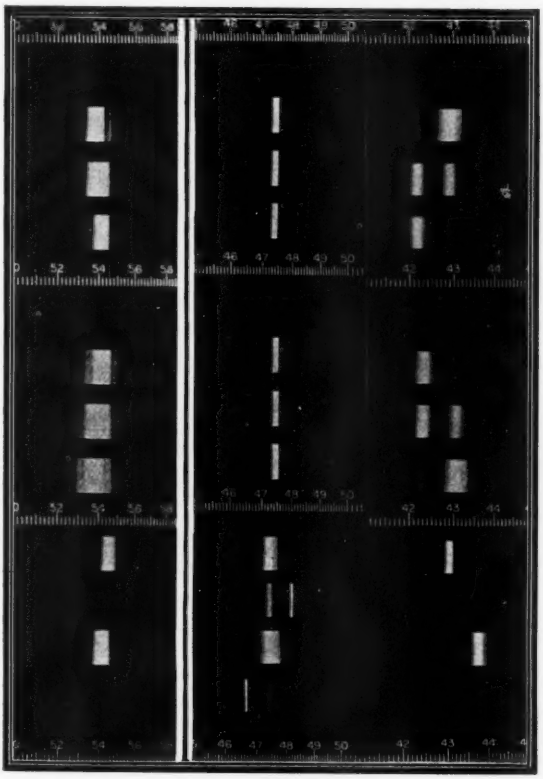
P0 A0

P90 A0

P90 A90

FIG. 1

A II B I B II



P90

P45

P0

A90

A45

A0

P0 A90

P0 A0

P90 A0

P90 A90

FIG. 2

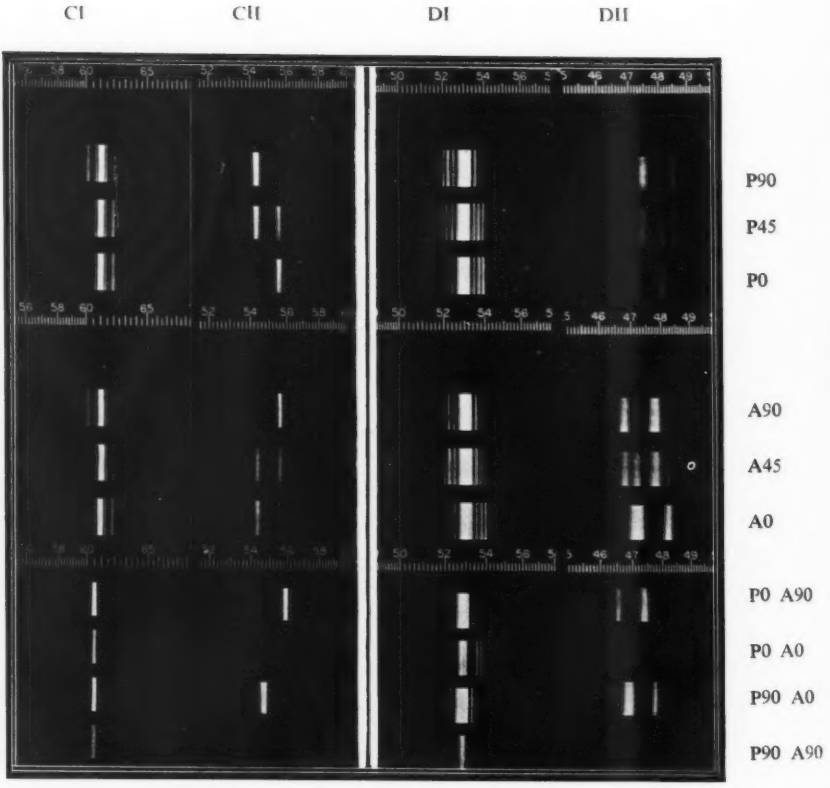


FIG 3

Figure C I.—The same remarks given for Figure B I apply to this figure also.

Figure C II.—The same remarks given for Figure B II apply to this figure also.

Figure D I.—The outer components of the triplet are themselves double. Otherwise the same remarks apply to this figure as in the case of Figures B I and C I.

Figure D II.—Each of the components is now double and the two subsidiary components behave in opposite ways. Otherwise the remarks are the same as in the case of B II and C II.

11. Summary

A simple explanation is given why the reflections vanish when the light is incident in the symmetry plane of the twinned crystals. Physical considerations enable the law of polarisation for twin-plane reflections to be derived for directions of incidence adjoining the plane of symmetry. It is further shown that the spectral character of the reflections stands in the closest relationship with the polarisation law thus derived. An explanation is given for the appearance of doublets and triplets respectively in the spectra observed when the incidence is oblique and the azimuth of such incidence is nearly zero and 90° respectively. It is a necessary consequence of the theory that the outer components in these two cases should be plane-polarised, in one case in the reciprocal fashion and in the other case normally. The theoretical results are strikingly confirmed by observations on the polarisation of the spectral components. Photographs are reproduced illustrating these effects.

ON THE IRIDESCENCE OF POTASSIUM CHLORATE CRYSTALS

Part III. Some General Observations

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Received November 3, 1952

1. Introduction

In the two preceding parts we have discussed the optical behaviour of a few selected crystals which could be regarded as ideal or nearly ideal specimens exhibiting highly monochromatic iridescence. It is not without interest however to consider the subject from a wider standpoint. It is proposed in the present part to report briefly on the optical phenomena observed by us in our studies with a rather extensive collection of specimens. The availability of the material was due to the circumstance that some years ago a chemical manufacturing concern at Bangalore was engaged in the large-scale production of potassium chlorate. Arrangements were made with them for a systematic collection of the iridescent crystals that occasionally formed in the crystallising vats.

A good way of exhibiting a collection of the iridescent crystals is to place the same on a flat circular disc of black glass held horizontally and which could be rotated about a vertical axis. The reflected colours can be viewed under the diffuse illumination provided by a large window. The variety and brilliance of the tints and their rapid change with the obliquity of observation then become strikingly evident; and the disappearance and the reappearance of the iridescence of each specimen twice in each revolution of the disc can also be exhibited. This arrangement, however, does not eliminate the dilution of the iridescence by the reflection of white light from the two surfaces of the crystal. This can only be secured by mounting the plates in Canada balsam between two prisms of glass. The liveliness of the colours is thereby vastly improved and the arrangement is also suitable for exhibiting the transmission colours in a very striking manner. It is also the most suitable arrangement for a critical spectroscopic study of the reflected or transmitted light. The simple technique of immersing the specimen in a watch glass containing xylene, the outside of which has been dead-blacked, however suffices for a rapid visual examination of numerous specimens. Indeed it may be used also for obtaining a photographic record of their spectra.

2. Characters of the Iridescence

The majority of the specimens are rhombus-shaped tablets, but hexagonal-shaped plates are also not infrequently met with. An impressive feature is the fact that though the individual crystals exhibit the widest diversity of colours by reflection, such colour is usually quite uniform over the area of a particular crystal. Occasionally however, one finds plates which exhibit iridescence of one colour over part of the area and either no iridescence at all or else an iridescence of a different colour or intensity over the rest of it; the dividing line between the two parts in such cases is usually sharp but rather wavy. Straight boundaries are however occasionally observed.

It is possible at first sight to believe that a particular specimen is non-iridescent and yet to discover on closer examination that it exhibits the characteristic reflections. This can happen, for instance, when the reflection is at the violet end of the spectrum at nearly normal incidence and moves out of the visible with oblique observation. It may also happen that the crystal has a series of monochromatic reflections in the visible spectrum the integrated effect of which is merely white light. There are cases also where the characteristic reflection moves into the visible spectrum and results in visible colour only when the crystal is viewed obliquely.

A systematic examination of the specimens was made to find whether any of the tablets have stratifications so fine that the first order reflection appears only in the ultra-violet. These were looked for by photographing a continuous spectrum of white light transmitted obliquely through the specimen. Though many crystals were examined, no such case was met with. *Prima facie* there seems to be no reason why such fine stratifications cannot appear, and it is possible they were not found merely because they had been passed over when the material was collected. On the other hand, crystals were forthcoming with stratifications so widely spaced that thirteen successive orders of reflections are observed between λ 6600 and λ 3200. This would mean that the order actually observed at the red end would be the twelfth, the first order being far out in the infra-red and that the actual spacing of the stratifications would be about $2 \cdot 7\,\mu$. On the other hand, a crystal showing a first order in the violet say at λ 4200 would have a spacing of $0 \cdot 14\,\mu$.

3. Variations of Its Spectral Nature

In Plate XIV, Figs. 1 to 8 are illustrated the reflection spectra taken at nearly normal incidence of a series of eight crystals, beginning with a specimen which shows a single reflection (probably a first order) at λ 4275, followed by others showing a large number of reflection maxima up to

thirteen. It is generally the case that if a crystal exhibits a series of monochromatic reflections, the monochromatism becomes sensibly more perfect in the higher order reflections seen in the ultra-violet. This feature is readily noticeable in several of the spectra reproduced in Plate XIV. It is also generally characteristic of monochromatic reflections that their intensity is far larger than that of the subsidiary maxima accompanying them, so much so that the latter are recorded only with prolonged exposures. We have however come across several cases in which a crystal gives a series of reflection maxima forming a regular sequence, but in which we do not observe the regularities referred to above. Some examples of this kind are reproduced as Figs. 6, 7 and 8 in Plate XIV. It will be seen in these three pictures that the reflection maxima are rather diffuse, each of them visibly exhibiting several components distinctly resolved from each other and that the structure of the individual reflections is not always the same. Further, the subsidiary maxima may often attain a notable intensity and show a lack of regularity in their distribution. This feature is very conspicuous in Fig. 8, Plate XIV. A natural explanation of the facts observed is that the stratifications are not perfectly equidistant in these cases but are subject to errors in spacing which may be either random or periodic.

Another interesting feature which is occasionally noticed is that some of the orders are unusually strong and others unusually weak in comparison with their neighbours, *e.g.*, the reflection at λ 5800 appearing in Fig. 6 in Plate XIV is very strong, whereas the order at λ 4850 is weaker than the orders on either side of it. Similarly in Fig. 4, Plate XIV, the orders appearing at λ 4350 and at λ 4900 are far stronger than the orders appearing on either side at λ 3950 and λ 5600 respectively. The latter is so weak that the principal maximum and the subsidiary maxima on either side are of nearly comparable intensity. Another example of the same kind is the reflection appearing at λ 4130 in Fig. 5, Plate XIV, which is much weaker than the orders at λ 3920 and λ 4380 respectively on either side. One more illustration is furnished by Fig. 7 in Plate XIV in which the reflection appearing at λ 4475 is far stronger than the orders at λ 4050 and λ 5000 respectively on either side, the latter being extremely weak. A natural explanation for these facts is to be found in the different thicknesses of the alternate layers of the polysynthetically twinned crystal. The ratio of these thicknesses would determine the relative intensity of the different orders of reflection.

4. MULTIPLY-PERIODIC TWINNING

In the course of our studies also, several examples were met with in which instead of a single series of sharply defined reflection maxima, regu-

larly spaced groups of such reflection maxima were obtained, the successive orders exhibiting almost identically similar features. Four such spectra are reproduced as Figs. 1 to 4 in Plate XV. The similarity of the successive groupings is particularly conspicuous in Fig. 4 in that plate, though it may be readily recognised in the others as well. In Fig. 1 in Plate XV the principal feature observed is a strong band centred at λ 6000 with other features on either side of it. The corresponding order in the violet is rather weak and exhibits a strong central band at λ 4050 and weak bands at λ 3820 and λ 4350 respectively which are hardly visible in the reproduction.

Two alternative views may be put forward regarding the structures responsible for such spectra. One is that each specimen contains several separate layers of iridescent material, each of which gives its own series of monochromatic reflections of different orders. While this view cannot be summarily rejected, it is rather difficult to reconcile with all the observational facts and it would, in particular, require a considerable thickness of the crystal to contain all the separate lamellæ required by such an explanation. Another view which appears to merit consideration is that the twinning in such crystals is multiply-periodic, in other words, that two or more sequences of equidistant planes exist side by side in the same layer. Such a structure would naturally give rise to complex groups of lines in the spectra instead of a single series of monochromatic reflections.

Finally, mention should also be made of cases which depart still further from the ideal structures giving monochromatic reflections. They give spectra in which the bulk of the intensity is concentrated in particular regions of the spectrum but not in the manner characteristic of regularly ordered stratifications. Examples of spectra of this type are reproduced as Figs. 5 to 8 in Plate XV.

5. Summary

The paper describes the results of a study of an extensive collection of material. The spacing of the stratifications giving rise to monochromatic reflections has been found to range from $2{\cdot}7\,\mu$ to $0{\cdot}14\,\mu$. The monochromatism becomes sensibly more perfect in the reflections of higher orders. Variations in intensity from order to order are also noticeable and these are ascribed to the alternate lamellæ in the twinning being of different thickness. Instead of a single series of monochromatic reflections, regularly spaced groups of reflection maxima are also observed in some cases. The components in each group of such reflections may be wide apart or else may be closely spaced. The nature of the stratifications in these cases is discussed.

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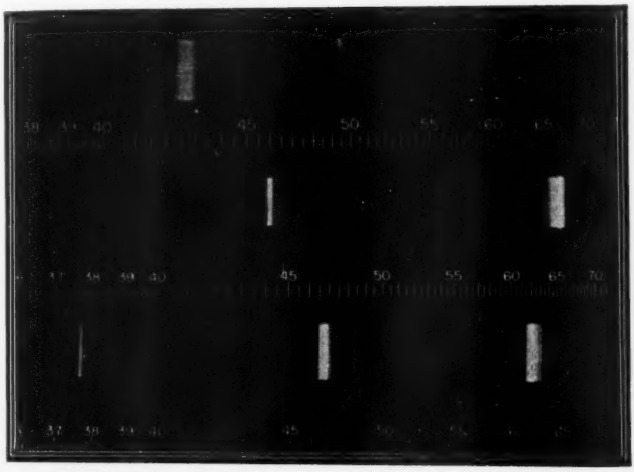

FIG. 1

FIG. 2

FIG. 3

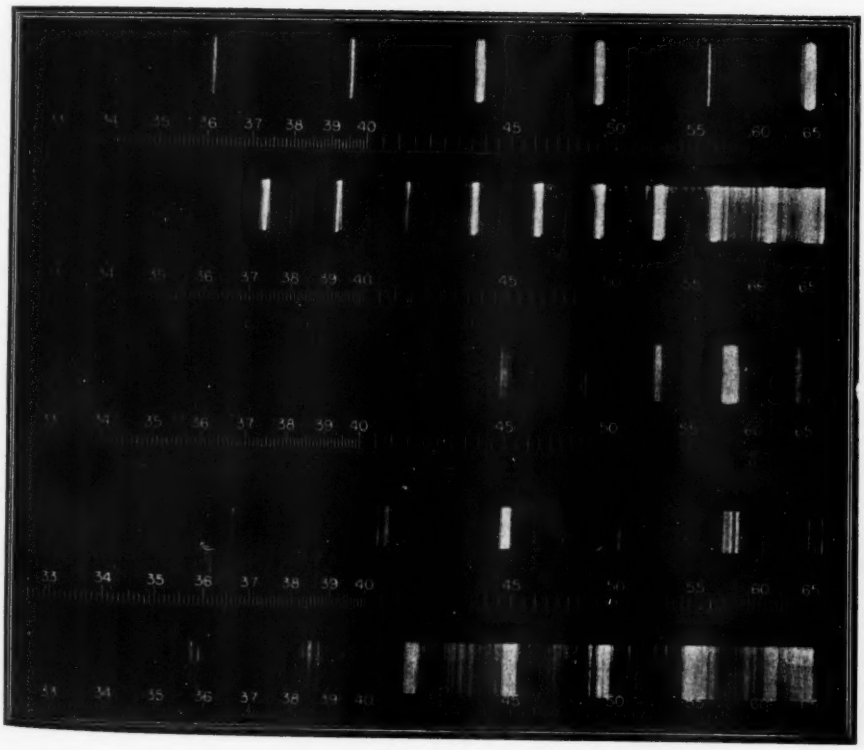

FIG. 4

FIG. 5

FIG. 6

FIG. 7

FIG. 8

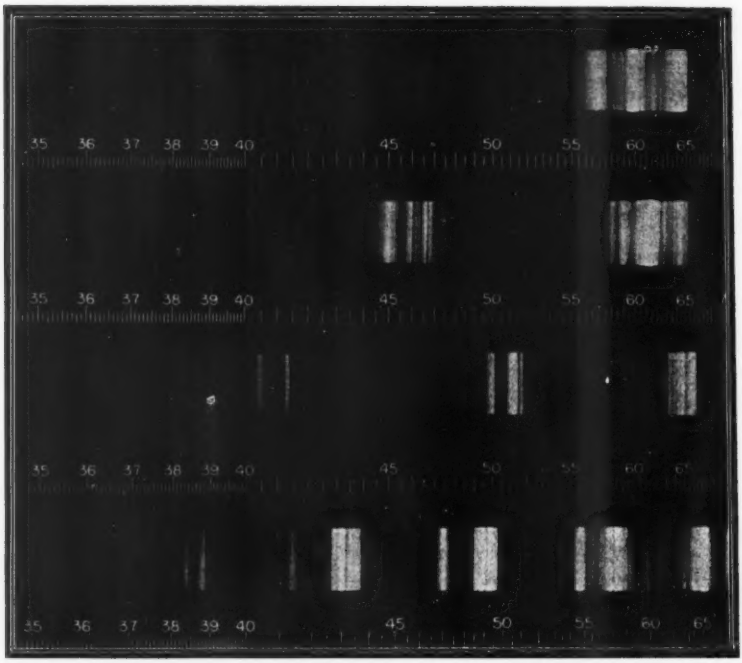

FIG. 1

FIG. 2

FIG. 3

FIG. 4

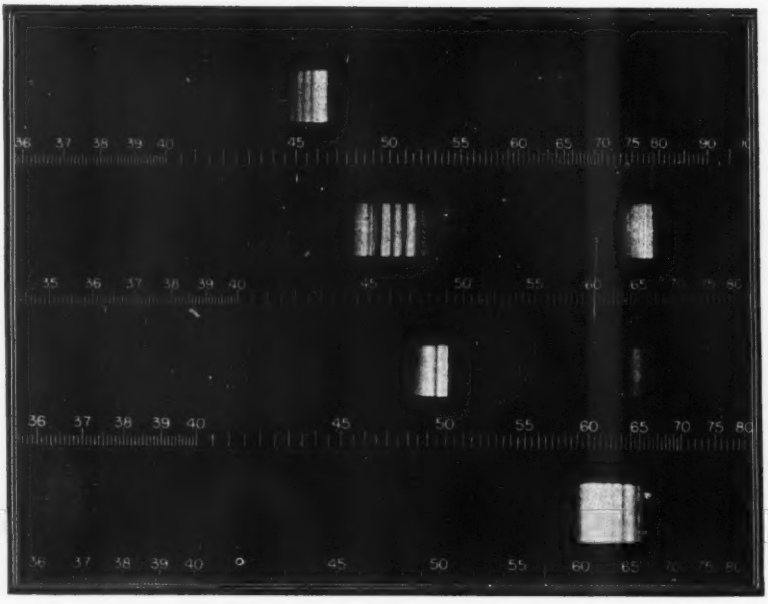

FIG. 5

FIG. 6

FIG. 7

FIG. 8

ON THE ASYMPTOTIC BEHAVIOUR OF SOLUTIONS OF NON-LINEAR DIFFERENTIAL EQUATIONS

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(Communicated by Dr. T. Venkatarayudu, F.A.SC.)

§1. Introduction

The aim of this paper is to develop a simple theory about the boundedness and asymptotic equilibria of solutions of non-linear differential equations. Norman Levinson[1] and Hermann Weyl[2] considered the boundedness of solutions of perturbed linear systems where the perturbations could be majorised by linear functions. Aurel Wintner[3, 4] considered the problem of asymptotic equilibria subject to certain conditions. We shall investigate sufficient conditions for the boundedness of solutions of non-linear differential equations and obtain a generalisation of the results of Aurel Wintner about asymptotic equilibria. The method suggested here is shown to be applicable to the case of non-linear perturbations as well.

In §2 we shall prove a lemma which will be useful for subsequent discussion. In §3 we consider a theorem which, in some cases, gives an upper bound to the difference between any two solutions of a differential equation passing through a point. In §4 we consider some comparison theorems which follow naturally from the lemma proved in §2 and deduce a generalisation of the results of Aurel Wintner about asymptotic equilibria. Finally in §5 we discuss the case of non-linear perturbations as an illustration of the above theorems. The last discussion generalises the results of Norman Levinson and Hermann Weyl referred to above.

§2

Lemma.—Suppose

(1) $f(x, y)$ is continuous and non-decreasing in y in the region G defined by $\xi \leqslant x \leqslant a$; $-\infty < y < +\infty$

(2) $y(x)$ is continuous in the interval $\xi \leqslant x \leqslant a$ such that $y(\xi) = \eta$ and satisfies the integral inequality

$$y(x) \leqslant \eta + \int_{\xi}^{x} f(x, y)\, dx$$

(3) $\phi(x)$ is the maximal solution of $z' = f(x, z)$ through (ξ, η); (x, z) in G.

Then

$$y(x) \leqslant \phi(x) \text{ for } \xi \leqslant x \leqslant a.$$

Proof.—Take $y(x)$ as the zero approximation to the solution of the differential equation $z' = f(x, z)$ through (ξ, η). We shall show by induction that the successive approximations form a monotonic increasing sequence. Suppose the k-th approximation is Z_k; and $Z_k \geqslant Z_{k-1}$. Then

$$Z_{k+1} - Z_k = \int_{\xi}^{x} \{f(x, Z_k) - f(x, Z_{k-1})\}\, dx$$

$$\geqslant 0 \text{ since } f(x, z) \text{ is non-decreasing in Z.}$$

But by (2) the zero approximation is less than the first approximation. So, the successive approximations form a monotonic increasing function sequence and since they are uniformly bounded and equicontinuous must converge uniformly to a function $\psi(x)$. Further it is clear that $\psi(x)$ is a solution of the differential equation through (ξ, η) and

$$y(x) \leqslant \psi(x) \text{ since the successive approximations are monotonic increasing}$$

$$\leqslant \phi(x), \text{ where } \phi(x) \text{ is the maximal solution through } (\xi, \eta)$$

Q.E.D.

Note.—A very special case of this lemma which was extensively used by Richard Bellman in considering the boundedness of solutions of linear differential equations and by Hermann Weyl[2] is as follows:—

$$\text{If} \quad |y(x)| \leqslant M\left(1 + k\int_0^x |f|\,|y|\,dt\right)$$

$$\text{then } |y(x)| \leqslant M \exp\left(kM\int_0^x |f(t)|\,dt\right).$$

This can be very easily deduced from the above lemma.

§3

The following theorem gives sometimes a bound on the difference between any two solutions (in particular the maximal and minimal solutions) of a differential equation through a given point.

3·1. THEOREM I. If

(1) $\omega(x, z)$ is continuous and $\geqslant 0$ in the region R defined by $\xi \leqslant x \leqslant a$; $z \geqslant 0$ and non-decreasing in z for fixed values of x in this interval;

(2) $|f(x, y_1) - f(x, y_2)| \leqslant \omega(x, |y_1 - y_2|)$;

(3) the maximal solution of $Z' = \omega(x, Z)$ through $(\xi, 0)$ is $\phi(x)$

then, the difference between any two solutions of the equation $y' = f(x, y)$ through (ξ, η) is $\leqslant \phi(x)$.

Proof.—Suppose any two solutions of the equation through (ξ, η) are $y_1(x)$ and $y_2(x)$. Then

$$|y_1 - y_2| \leqslant \int_{\xi}^{x} |f(x, y_1) - f(x, y_2)| \, dx$$

$$\leqslant \int_{\xi}^{x} \omega(x, |y_1 - y_2|) \, dx.$$

Putting $|y_1 - y_2| = z$ and applying the lemma we get

$$|y_1 - y_2| \leqslant \phi(x)$$

Q.E.D.

3·2. The monotonic increasing character of $\omega(x, z)$ in the above theorem can be entirely relaxed and the theorem is still true as can be demonstrated as follows:—

Suppose $\phi(x, \epsilon)$ is a solution of $z' = \omega(x, z) + \epsilon$ through $(\xi, 0)$, where ϵ is a small positive quantity. The maximal solution of $z' = \omega(x, z)$ through $(\xi, 0)$ is given by $\lim_{\epsilon \to 0} \phi(x, \epsilon)$. *See* [5]. Hence it is enough to show that for all sufficiently small values of ϵ

$$|y_1(x) - y_2(x)| \leqslant \phi(x, \epsilon).$$

Now, this inequality is satisfied at the point ξ. Suppose at a point x it is not satisfied. Then, on account of the continuity of all the functions involved, there is a greatest open interval in which this is not satisfied. Let this interval be $\xi \leqslant \alpha < x < \beta$. At α and β the above relation reduces to equality. In other words

$$|y_1(\alpha) - y_2(\alpha)| = \phi(\alpha, \epsilon) \text{ and}$$

$$|y_1(x) - y_2(x)| > \phi(x, \epsilon) \text{ for } \xi \leqslant \alpha < x < \beta.$$

Taking the right-hand derivative at α

$$|y_1'(\alpha) - y_2'(\alpha)| \geqslant |y_1(\alpha) - y_2(\alpha)|' > \phi'(\alpha, \epsilon).$$

Therefore, $$|f[\alpha, y_1(\alpha)] - f[\alpha, y_2(\alpha)]| > \omega[\alpha, \phi(\alpha, \epsilon)] + \epsilon$$

$$\therefore \quad \omega(\alpha, |y_1(\alpha) - y_2(\alpha)|) > \omega[\alpha, \phi(\alpha, \epsilon)] + \epsilon$$

which is a contradiction since $|y_1(\alpha) - y_2(\alpha)| = \phi(\alpha, \epsilon)$.

Hence

$$| y_1(x) - y_2(x) | \leqslant \phi(x, \epsilon)$$

Q.E.D.

Note.—It should be carefully noted that this bound is independent of η and hence is the same at all points on the line $x = \xi$.

Corollary.—If G is taken to be the half plane to the right of the y axis, if $\phi(x)$ is bounded as $x \to \infty$ and if any one of the solutions of the differential equation $y' = f(x, y)$ through (ξ, η) is known to be bounded then every other solution is also bounded.

§4

In what follows we shall take the domain G as defined by $\xi \leqslant x < \infty$; $-\infty < y < +\infty$ and the domain R as defined by $\xi \leqslant x < \infty$; $y \geqslant 0$.

4·1. THEOREM II.—Suppose $y' = f(x, y)$ and $z' = g(x, z)$ are two differential equations with (x, y) and (x, z) in G satisfying the following conditions:

(1) $| f(x, y) - g(x, z) | \leqslant \omega(x, | y - z |)$,

(2) $\omega(x, z)$ is continuous, $\geqslant 0$ and non-decreasing in z in the region R,

(3) $\phi(x)$ is the maximal solution of $\chi' = \omega(x, \chi)$ through $(\xi, 0)$ and $\lim_{x \to \infty} \phi(x) < \infty$,

(4) Any solution of one of the equations through (ξ, η) is bounded, then, any solution of the other equation through (ξ, η) is also bounded.

Proof.—The solutions of the two equations are given by

$$y = \eta + \int_{\xi}^{x} f(x, y)\, dx \quad \text{and} \quad z = \eta + \int_{\xi}^{x} g(x, z)\, dx.$$

Therefore

$$| y - z | \leqslant \int_{\xi}^{x} | f(x, y) - g(x, z) |\, dx$$

$$\leqslant \int_{\xi}^{x} \omega(x, | y - z |)\, dx.$$

Applying the lemma, we at once get $| y - z | \leqslant \phi(x)$ and the result follows on account of (3) and (4) of the theorem.

Q.E.D.

We shall now consider systems of differential equations. We shall consider $y' = f(x, y)$ where y and f are column vectors of n components each. The norm of a vector y is defined as $\sum_{i=1}^{n} | y_i |$ and denoted by $\| y \|$. This

satisfies the usual requirements of a norm. We shall say that a vector is bounded when its norm is bounded.

4·2. THEOREM III.—If in the differential system $y' = f(x, y)$

(1) $\| f(x, y) \| \leqslant \omega(x, \| y \|)$

(2) $\omega(x, z)$ is continuous; $\geqslant 0$ and non-decreasing in z in R for fixed values of x

(3) The maximal solution $\phi(x)$ of $z' = \omega(x, z)$ through $(\xi, \| \eta \|)$ is bounded as $x \to \infty$

(4) $y(x)$ is a solution vector of $y' = f(x, y)$ through (ξ, η) then,

$$\lim_{x \to \infty} \| y(x) \| < \infty$$

Proof.—The solution vector of the given system is given by

$$y = \eta + \int_{\xi}^{x} f(x, y)\, dx$$

Therefore

$$\| y \| \leqslant \| \eta \| + \int_{\xi}^{x} \| f(x, y) \|\, dx$$

$$\leqslant \| \eta \| + \int_{\xi}^{x} \omega(x, \| y \|)\, dx.$$

Applying the lemma, on account of (3) we get

$$\| y \| \leqslant \phi(x).$$

The conclusion follows immediately on account of (3).

Q.E.D.

4·3. THEOREM IV.—Suppose $\omega(x, z)$ of Theorem III has the property $\int^{\infty} (x, \mathrm{M})\, dx < \infty$ for arbitrarily fixed M. Then every solution vector through (ξ, η) tends to a finite limit as $x \to \infty$, a case of asymptotic equilibrium.

Proof.—Suppose M is the upper bound of $\| y(x) \|$ and since $\omega(x, z)$ is non-decreasing in z

$$\| \frac{dy}{dx} \| = \| f(x, y) \| \leqslant \omega(x, \| y \|) \leqslant \omega(x, \mathrm{M})$$

$$\therefore \int^{\infty} \| \frac{dy}{dx} \|\, dx \leqslant \int^{\infty} \omega(x, \mathrm{M})\, dx < \infty$$

This implies

$$\int^{\infty} \left| \frac{dy}{dx} \right| < \infty \text{ for } i = 1, 2, 3, \ldots\ldots, n$$

which in its turn implies that $y_i(x)$ tends to a finite limit as $x \to \infty$ for $i = 1, 2, 3, \ldots\ldots, n$.

Q.E.D.

Note.—Aurel Wintner considered the problem of asymptotic equilibrium in [3] and [4]. The result he proved in [3] is as follows:—

If

$$(1)\ \int_{\bullet}^{\infty} f_i(t, 0, 0, 0, \ldots\ldots)\, dt < \infty \text{ for } i = 1, 2, 3, \ldots\ldots, n$$

$$(2)\ |f_i(t, x_1^1, x_2^1, x_3^1 \ldots\ldots) - f_i(t, x_1^2, x_2^2, x_3^2 \ldots\ldots$$

$$\leqslant \sum_{k=1}^{n} \lambda_{ik}(t)\, |x_k^1 - x_k^2| \text{ for } i = 1, 2, 3, \ldots\ldots, n$$

$$(3)\ \int^{\infty} \lambda_{ik}(t)\, dt < \infty \text{ for } i, k = 1, 2, 3, \ldots\ldots, n.$$

Then each solution of the equation tends to a finite limit as $t \to \infty$.

In [4] he generalised the above theorem to the following case.

$$|f(t, x)| < \lambda(t)\, \phi(|x|),$$

where $\lambda(r)$ and $\phi(r)$ are both positive for $0 \leqslant r < \infty$; continuous for $0 < r < \infty$ and satisfy the conditions

$$\int^{\infty} \lambda(t)\, dt < \infty \text{ and } \int^{\infty} \frac{dr}{\phi(r)} = \infty.$$

The case considered by us is more general in the respect that we do not assume the product form for $\omega(x, z)$. Further we do not assume the stronger Lipschitz's condition for $f(x, y)$.

§5

As an illustration of the foregoing discussion, we shall consider the problem of non-linear perturbations.

5·1. Let the perturbed equation be

$$(A)\quad z_i' = \sum_{j=1}^{n} a_{ij} z_j + f_i(z_1, z_2, z_3, \ldots\ldots, t) \qquad i = 1, 2, \ldots\ldots, n$$

Following Hermann Weyl[3] we can write this equation symbolically as $z' = Az + f(z, t)$, where z and f are column vectors of n components each and A is a $n \times n$ matrix. We shall suppose that the elements of the matrix are constants. We shall say that a matrix A is bounded if $\|A\|$ *i.e.*, $\sum_{j=1}^{n} |a_{ij}|$ is bounded.

Any solution of the equation (A) with $z(0) = y_0$ is a solution of the integral equation.

(B) $\mathrm{Z} = y + \int_0^t \mathrm{Y}(t-s) f(z, s)\, ds$,

where $y(t)$ is a solution of the equation $\frac{dy}{dt} = \mathrm{A}y$ and Y is a solution of the matrix differential equation $\frac{d\mathrm{Y}}{dt} = \mathrm{AY}$; $\mathrm{Y}(0) = \mathrm{E}$ (unit matrix). y is a vector and Y is a matrix.

For proof *see* (2).

Further

$$\| y(t) \| = \| \mathrm{Y}(t)\, y_0 \| \leqslant \| \mathrm{Y}(t) \|\, \| y_0 \|.$$

Suppose now the following conditions are satisfied:

(1) $\| \mathrm{Y}(t) \| \leqslant a$ for $t \geqslant 0$

(2) $\| f(z, t) \| \leqslant \omega(\| z \|, t)$,

where $\omega(x, t)$ is non-negative, continuous, and non-decreasing in x for fixed values of t in the region R.

(3) The maximal solution $\phi(t)$ of the equation $z' = a\omega(z, t)$ through the point $(0, a \| y_0 \|)$ is bounded as $t \to \infty$, then, every solution of (A) is bounded as $t \to \infty$.

Proof.—From (B) we get

$$\| \mathrm{Z} \| \leqslant \| y \| + \int_0^t \| \mathrm{Y}(t-s) \|\, \| f(z, s) \|\, ds$$

$$\leqslant a \| y_0 \| + a \int_0^t \omega(\| z \|, s)\, ds$$

$\therefore \quad \| z \| \leqslant \phi(t)$ and the conclusion follows immediately on account of (3).

5·2. If $\omega(z, t)$ is such that it satisfies the condition $\int_0^\infty \omega(\mathrm{M}, t)\, dt < \infty$ or arbitrarily fixed M, then we can always split up $z(t)$, any solution of (A) into two parts $z_1(t)$ and $z_2(t)$ such that $z_1(t)$ tends to zero with $t \to \infty$ and there exists a solution $x_1(t)$ of the simple equation $x_i'(t) = \sum_{j=1}^{n} a_{ij}\, x_j$ $(i = 1, 2, \ldots, n)$ such that $z_1(t) - x_1(t) = 0$ for $t = 0$ and $z_2(t) - x_2(t) \to 0$ for $t \to \infty$.

Proof.—Suppose $\| z(t) \| \leqslant \mathrm{M}$ and $\int_0^\infty \omega(\mathrm{M}, t)\, dt = q$

then $\| f(z, t) \| \leqslant \omega(\| z \|, t) \leqslant \omega(\mathrm{M}, t)$.

With the above proviso, the proof of the theorem is the same as that given by Hermann Weyl[2] for linear perturbations and is therefore omitted.

Note.—Norman Levinson[1] and Hermann Weyl[2] assumed $\omega(z, t)$ to be of the form $q(t)\, z$, where $\int_0^\infty q(t)\, dt < \infty$. The form considered here is more general in the respect that the perturbations could be majorised by non-linear functions, not necessarily of the product form.

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SURFACE FILMS OF INVERTASE

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Introduction

Invertase is an enzyme which hydrolyses sucrose into glucose and fructose. It is also known by the names invertin, saccharase and sucrase. The invertase obtained from yeast is known to be β-4-fructosidase. The molecular weight is supposed to be 20,000, iso-electric point is supposed to be 5·0, phosphorus is present in traces.[1, 2, 3] The nitrogen content is variable and values from 6·6–12·7% are reported. Only part of nitrogen is in the form of amino nitrogen and Willstaetter and Schreider[1, 2, 3] express doubts as to its protein nature. On the other hand, the presence of polypeptides seems probable.

It is not clear whether the agon representing the active group of the enzyme and the pheron the carrier, are combined to form a specific protein or whether the agon is merely absorbed by the pheron. The pheron in this case appears to be an ampholyte containing nitrogen.[4]

Recent work by Gorter and Dieu has shown that two constituents are present in purified invertase, one of them having a low molecular weight of the order of 3,500 and the other of high molecular weight of the order of 100,000, the former being considered responsible for invertase activity. These authors have also made a study of the spreading behaviour of invertase.

The object of the present investigation is to study the spreading behaviour of commercial invertase over various substrata. Further a special technique has been adopted for investigating the mechanism of variation of spreading with pH.

Experimental

Apparatus used.—The film balance was improvised using du NOUY tensiometer.[5] The trough used for filling the solution was made by fixing

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glass strips on a glass plate by means of paraffin wax. Paraffined glass strips were used as barriers for handling the film. The entire apparatus was enclosed in a glass cabinet to avoid contamination of the substratum.

Materials used.—(1) Sample of invertase used was supplied by Messrs. Sugar Manufacturers' Supply Co., Ltd., 7–8, Idol Lane, London. As per details kindly supplied by the Firm, the invertase was prepared from Baker's yeast, carefully purified and stabilised by using purest glycerine and has been certified as not containing any other surface-active substance or nitrogenous substance.

(2) Ammonium sulphate, barium chloride and trichloracetic acid used were of A. R. quality.

(3) *Sodium Metaphosphate.*—This was prepared by heating microcosmic salt in a platinum dish at red heat. The red hot dish was carefully quenched in water and the solid metaphosphate stored in a dry bottle.

(4) *Formalised Invertase.*—Equal quantities by volume of invertase and freshly distilled 40% formalin were mixed and the mixture was allowed to stand for two days.

(5) *Invert Sugar.*—This was prepared by using the method given by Zerban and Browne.[6] Sucrose used was a Merck product of C.P. quality.

The various buffer solutions were prepared from chemicals of C.P. quality and the pH was measured by quinhydrone electrode.

Determination of Nitrogen Content of Invertase.—Nitrogen content of the invertase sample was determined by Kjeldahl's method and it was found to be $0{\cdot}65 \pm 0{\cdot}06$ mg./c.c. The absolute values of the area per mg. are based on this value and hence are accurate to only 10%.

Determination of Time Value.—A standard sucrose solution is treated with measured quantity of invertase at the optimum pH. After incubation at a definite temperature, samples are removed at regular intervals and degree of hydrolysis determined.[7] The time value of the invertase sample was found to be 58 minutes.

Technique of Spreading.—The essential requirement for studying the surface behaviour of invertase is a reliable and reproducible method of spreading the invertase. Invertase being soluble in water, there is always a risk of the protein going into the bulk of the substratum during the process

of spreading. A large number of methods have been used for spreading proteins by various workers in the field. Gorter and Grendel[8] forced the solution through a capillary kept horizontal and close to the surface. Fourt and Schmidt[9] used micrometer syringe and kept the needle just above the surface and in contact with it. Neurath[10] on the other hand prefers to drop the solution from a height of 2–3 mm. Langmuir and Co-workers spread the protein by taking its solution in the form of a band on a metal foil and slowly lowering the foil into the substratum.

The method used in the present work for spreading the invertase is a modification of the Langmuir method. Two glass strips about 6″ long and 1″ wide were coated with paraffin, upto 2″ from one end. The strips were handled by the paraffined ends so that any surface-active impurities from the hand may not pass on to the liquid on the glass strip. The bare portions of the strips were cleaned by warm chromic acid and washing with distilled water. A small quantity of the solution of invertase, measured by the Agla micrometer syringe was put on one of the strips and worked into a thin film with the other strip. The strips were then slowly lowered into the substratum the surface of which had been cleaned by barriers. The strips were then slowly rotated so that all the sides came in contact with the liquid. The strips were then taken out of the substratum. This technique has given satisfactory results.

To test the purity of the strips a blank was performed with the strips only and the area occupied by the film of impurities at a surface pressure of 1 dyne/cm. was measured. This was found to be less than 2% of the original area swept for spreading. In some extreme cases the impurity of the surface was of the order of 5% of the area swept.

Results

Force-area curves were obtained for invertase films over substrata of different pH from 1·0 to 7·0. Further substrata containing substances which are known to interact with proteins such as trichloracetic acid and sodium metaphosphate were also used. Effects of the presence of ammonium sulphate, barium chloride and invert sugar in the substratum were examined. Effect of heat and treatment with formaldehyde on the spreading of invertase has been examined. A few typical force-area curves are given. The effects of the various substrata etc., have been expressed by giving the respective areas per mg. of nitrogen of the invertase film at 2 dynes/cm. pressure. All the experiments were done in triplicate and the average values are given in the tables below:

Table I

Effect of pH on Spreading of Invertase

pH	Substratum	Area at 2 dynes/cm. sq. metres/mg. nitrogen
1·0	Hydrochloric acid 0·1 N	1·58
1·5	„ „ (dilute)	0·24
2·0	„ „ 0·01 N	0·14
3·0	„ „ 0·001 N	0·097
3·5	„ „ (dilute)	0·083
3·5	Sodium acetate and Acetic acid buffer	0·080
4·0	„ „ „ „	0·115
4·5	„ „ „ „	0·111
5·0	„ „ „ „	0·103
5·5	„ „ „ „	0·098
7·0	Sodium phosphate and Citric acid buffer	0·08
6·8	Distilled water	0·07

Table II

Effect of Sodium Metaphosphate on Spreading of Invertase

pH	Substratum	Area at 2 dynes/cm. sq. metres/mg. nitrogen
1·0	0% Sodium metaphosphate in 0·1 N HCl	1·58
1·0	0·02% „ „ „	1·25
1·0	0·2% „ „ „	1·22
1·0	0·5% „ „ „	0·98
1·0	1·0% „ „ „	1·03
1·0	2·0% „ „ „	1·06
3·0	0·2% „ „ „	0·097
3·0	0·5% „ „ in dilute HCl	0·16
3·0	1·0% „ „ „	0·156

TABLE III

Effect of Trichloracetic Acid on Spreading of Invertase

pH	Substratum	Area at 2 dynes/cm. sq. metres/mg. nitrogen
1·0	0% Trichloracetic acid in HCl	1·58
1·0	0·5% ,, ,, ,,	1·48
1·0	4·2% ,, ,, ,,	1·45
2·0	0% ,, ,, ,,	0·14
2·0	0·5% ,, ,, in distilled water	0·28

TABLE IV

Effect of Salts on Spreading of Invertase

pH	Substratum	Area at 2 dynes/cm. sq. metres/mg. nitrogen
1·0	8·75% Ammonium sulphate in 0·1 N HCl	1·36
1·0	12·5% ,, ,, ,,	1·34
1·0	17·5% ,, ,, ,,	1·07
1·0	25% ,, ,, ,,	1·06
1·0	35% ,, ,, ,,	1·35
3·0	8·75% ,, ,, in 0·001 N HCl	0·21
3·0	12·5% ,, ,, ,,	0·26
3·0	17·5% ,, ,, ,,	0·24
3·0	25% ,, ,, ,,	0·35
5·05	0·1 N Barium chloride in distilled water	0·44
5·05	0·5 N ,, ,, ,,	0·65

Table V

Effect of Invert Sugar on Spreading of Invertase

pH	Substratum	Area at 2 dynes/cm. sq. metres/mg. nitrogen
0·3	Hydrochloric acid	1·48
0·3	Invert sugar	1·55

Table VI

Effect of Heat on Spreading of Invertase

pH	Substance spread	Substratum	Area at 2 dynes/cm. sq. metres/mg. nitrogen
1·0	Unheated invertase	Hydrochloric acid 0·1 N	1·58
1·0	Heated invertase	,,	1·71

Table VII

Effect of Formaldehyde on Spreading of Invertase

pH	Substance spread	Substratum	Area at 2 dynes/cm. sq. metres/mg. nitrogen
1·0	Pure invertase	Hydrochloric acid 0·1 N	1·58
1·0	Formalised invertase	,,	0·61

Discussion

1. *Effect of pH on Spreading.*—The spreading is found to fall with rise in pH. The fall being very steep from pH 1·0 to 2·0 and thereafter it is nearly flat, though there is a slight indication of a flat maximum at about pH 4·5. The dependence of spreading on pH is a general feature exhibited

by many proteins. The question arises as to how spreading is affected by pH. One possibility is that at low pH the film is highly positively charged and by mutual repulsion spreads to a large area. The second possibility is that a good portion of the spread material may get into solution at higher

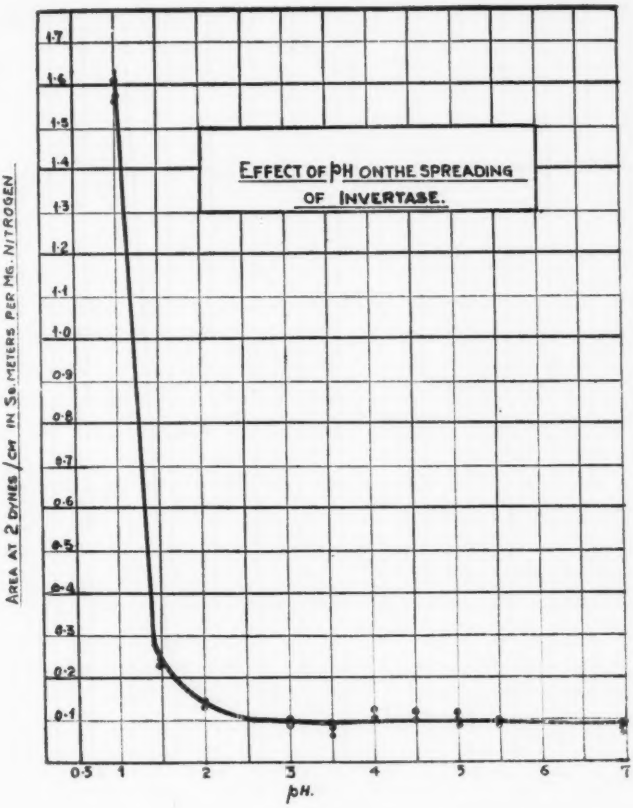

FIG. 1

pH values owing to the lower surface activity at high pH. To decide between the two alternatives a special technique was devised as described in the following section.

2. *The Technique for Investigating the Mechanism of the Action of pH on Spreading.*—ABCD is a trough (Fig. 2) constructed by fixing a beading of glass strips over a glass plate. EF is the float with thin paraffined silver ribbons. The float is as usual connected to the torsion balance for measuring the surface pressures. GH is a partition obtained by fixing a glass strip

by means of paraffin wax; this enables two different solutions to be taken in two portions AGHD and GBCH. Normally AGHD contains distilled water. In the first procedure, GBCH contains a solution of hydrochloric

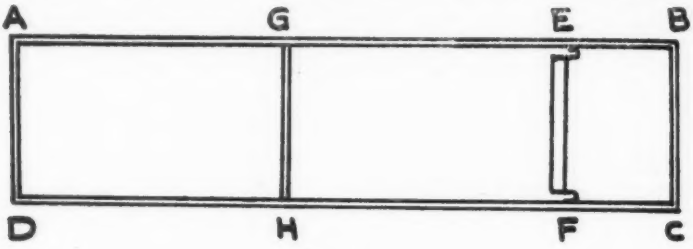

Fig. 2

acid having a pH 1·0. After cleaning with barriers the invertase film is spread over the area GEFH. The film is compressed towards the float by a barrier to a surface pressure of 2 dynes/cm. as indicated by the torsion balance. The area is measured. By manipulating by means of barrier the liquid surfaces AGHD and GBCH are made to unite over the partition GH. The invertase film is transferred to the water surface in AGHD. By again manipulating by means of a barrier the liquids in the two compartments are isolated. The hydrochloric acid in the compartment GBCH is sucked out. It is then washed with distilled water and filled with solution of pH 3·0. The top surface of this solution is made to come into contact with the distilled water surface over the barrier GH. The film which is over AGHD and which has been rinsed with water is slowly pushed to the buffer surface in the area GEFH. The film is then compressed to a surface pressure of 2 dynes/cm. and the area measured. In the second procedure the film is spread on a buffer surface of pH 3·0 in GBCH, shifted to water surface in the compartment AGHD and brought back to the surface of hydrochloric acid pH 1·0 in the compartment GBCH and the area measured at a surface pressure of 2 dynes/cm. The results are given below:

Procedure I

Transfer of the Film from pH 1·0 to pH 3·0

Experiment No.	Area at 2 dynes/cm. 0·1 N HCl, pH = 1·0	Area at 2 dynes/cm. 0·001 N HCl, pH = 3·0
1	0·99 sq. m./mg. nitrogen	1·45 sq. m./mg. nitrogen
2	0·92 „	1·37 „
3	0·95 „	1·37 „

PROCEDURE II

Experiment No.	Area at 2 dynes/cm. 0·001 N HCl, pH = 3·0	Area at 2 dynes/cm. 0·1 N HCl, pH = 1·0
1	0·108 sq. m./mg. nitrogen	0·25 sq. m./mg. nitrogen
2	0·106 ,,	0·24 ,,
3	0·108 ,,	0·30 ,,
4	0·11 ,,	0·33 ,,
5	0·09 ,,	0·27 ,,

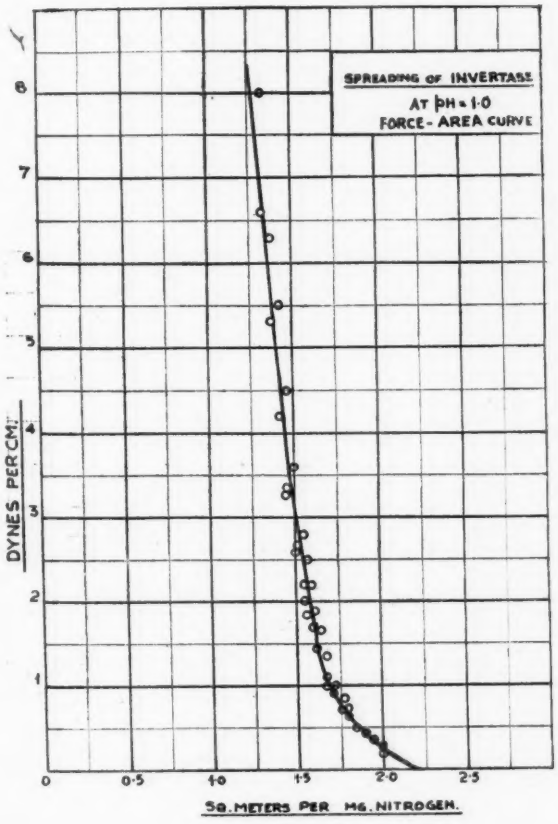

FIG. 3

An examination of Fig. 1 shows that the area at 2 dynes/cm. should increase about 16-fold as the film is shifted from pH 3·0 to pH 1·0 and correspondingly decrease when the film is shifted from pH 1·0 to pH 3·0. The observed results show that there is only a relatively small increase of

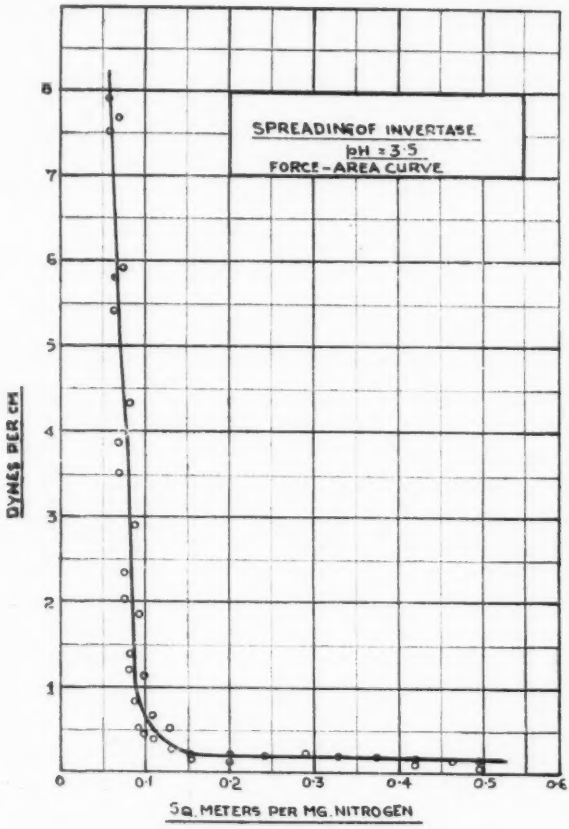

Fig. 4

area irrespective of the order in which the shift is carried out. Even this increase is presumably due to impurities introduced during the operation. This has been confirmed by blank experiments in which the film was spread on substrata of pH 1·0 and shifted after washing to the same substratum. The change in the area is again of the same order. These observations show (1) that the large difference in spreading is due to the invertase becoming less surface-active at higher pH so much so a large proportion of the

spread material would enter the solution below and (2) that a film once spread would not be dissolved by a substratum of higher pH. Perhaps there is a sort of irreversible denaturation during the spreading.

This technique which has given a clear picture of the mechanism of the action of pH on spreading with invertase and albumin[12] will be a valuable tool in all similar researches.

3. *Effect of the Composition of the Substratum on Spreading of Invertase.*—An examination of Table II shows that sodium metaphosphate has a contracting effect on the film at pH 1·0. This may be due to the metaphosphate increasing the lateral adhesion between the neighbouring points in the film. On pH 3·0 however the area per mg. increases by the action of this salt. It has already been seen that at pH 3·0 the apparent low spreading is due to a good proportion of the spread material going to the bulk of the solution. The sodium metaphosphate has a tendency to make the protein less soluble. Hence the tendency of the spread material to go into the substratum is diminished and thereby increases the apparent area.

The effect of trichloracetic acid is very similar to that of sodium metaphosphate.

The effect of ammonium sulphate is interesting. At pH 1·0 the contracting effect may be due to the lateral electrical repulsion being diminished by the high salt concentration. A very high percentage (35%) however appears to again increase the spreading. At pH 3·0 ammonium sulphate definitely increases the area which is presumably due to lowering of the tendency of the spread material getting into the substratum. Barium chloride tremendously increases the spreading area (at pH of 5·05) even at as low a concentration as 0·1 N. At 0·5 N concentration the effect is even more marked and there is more than 6-fold increase in the area. This is again due to diminishing of the solubility of invertase.

Invert sugar has practically no effect on the spreading of invertase. This is somewhat unexpected as the invert sugar is expected to be strongly adsorbed by invertase.

4. *Effect of Pretreatment of Invertase on Spreading.*—Heating the invertase for half an hour at 100° C. is found to slightly increase the spreading though the invertase activity itself becomes zero.

The effect of formalising invertase by treating it with excess of formaldehyde for 48 hours reduce the spreading tremendously. This is presumably due to methylene bridges developed during the treatment.

Acknowledgement

The authors wish to thank Professor J. M. Saha, Director, Indian Institute of Sugar Technology, Kanpur, for his kind interest in the work. Our thanks are also due to Professor J. P. Shukla, Biochemist, Indian Institute of Sugar Technology, for the facilities provided for the estimation of nitrogen, etc., in the sample.

Summary

1. A new technique has been described for studying the mechanism of action of pH on spreading of invertase. The film of invertase on 0·1 N HCl pH 1·0 was transferred to buffer solution pH 3·0 after washing it with distilled water. In the second experiment the film was spread on buffer of pH 3·0 and brought to 0·1 N HCl pH 1·0.

2. Sodium metaphosphate and trichloracetic acid have a contracting effect on the film at low pH but at higher pH the spreading is increased because the tendency of the film to dissolve at higher pH is reduced by these precipitants.

3. Ammonium sulphate at low pH has got a contracting effect but at higher pH this also increases the spreading. Barium chloride however increases the spreading considerably.

4. Invert sugar has been found to have no effect on the spreading of invertase.

5. Heating of invertase makes it completely inactive but the spreading is found to increase.

6. Treatment of the invertase with formaldehyde causes a decrease in spreading.

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NUCLEAR OXIDATION IN FLAVONES AND RELATED COMPOUNDS

Part XLI. A Study of 2′ : 5′-Hydroxy-Flavonols

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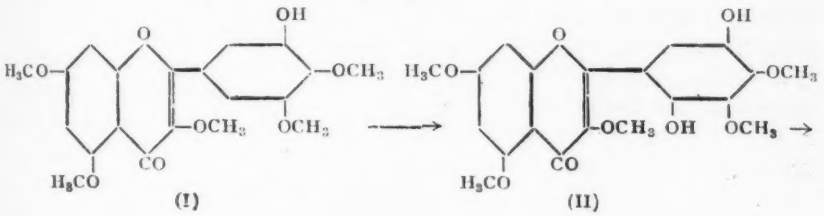
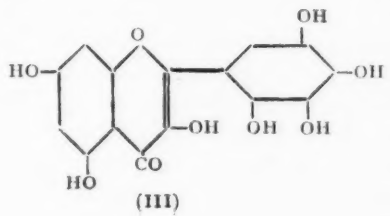
(Received September 22, 1952)

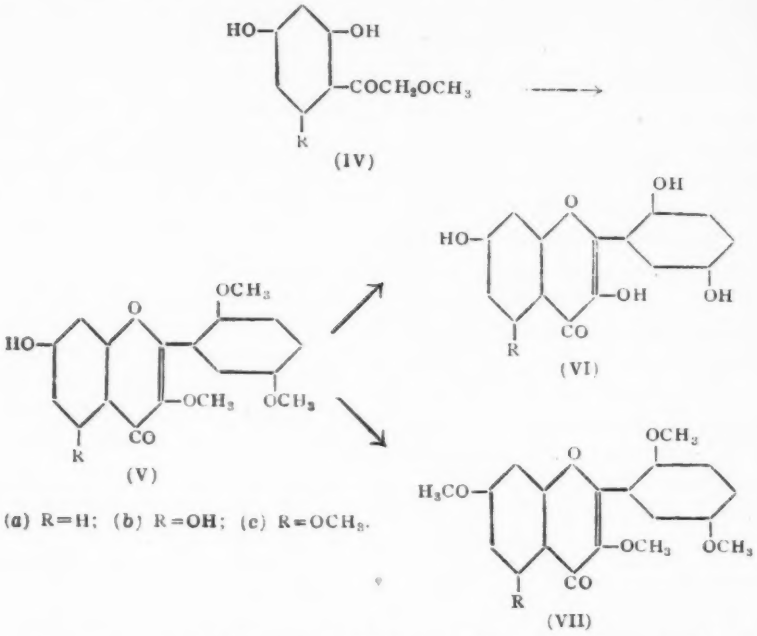
IN Part XXXIV[1] the first example involving para-nuclear oxidation in the side phenyl nucleus of the flavone structure was described. 3′-Hydroxy-3:5:7:4′:5′-pentamethoxy flavone (I) obtained from the glucoside cannabiscitrin was oxidised with persulphate to the 3′:6′-dihydroxy compound (II) and by subsequent demethylation the corresponding hepta-hydroxy flavone was secured (III). It was noticed that in regard to the alkali colour reactions the introduction of the para-dihydroxy grouping did not produce any marked difference as in similar cases involving the condensed benzene ring. In order to get more information on the influence of the dihydroxyl groups in the side phenyl nucleus simpler examples have now been prepared. These are 3:7:2′:5′-tetra-hydroxy flavone (VI *a*) and 3:5:7:2′:5′-penta-hydroxy flavone (VI *b*). They have been obtained by flavone synthesis in which ω-methoxy resacetophenone (IV *a*) and ω-methoxy-phloroacetophenone (IV *b*) are condensed with the anhydride and the sodium salt of gentisic acid dimethyl ether.



(I) (II)



(III)



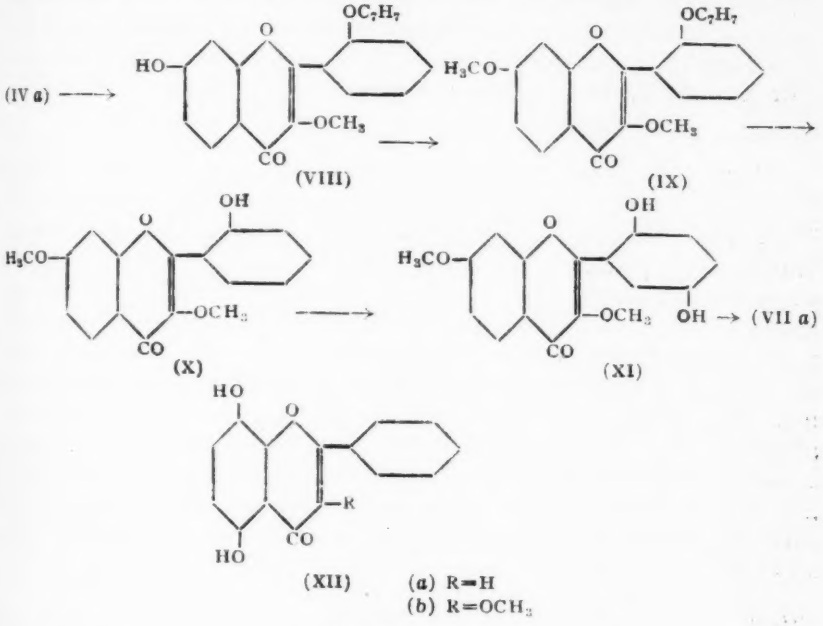
(*a*) R=H; (*b*) R=OH; (*c*) R=OCH_3.

The resorcinol derivative (VII *a*) has also been independently prepared using the method of nuclear oxidation. The stages are as follows:

ω-Methoxy resacetophenone (IV *a*) is condensed with the anhydride of 2-benzyloxy benzoic acid and its sodium salt. The resulting 7-hydroxy-3-methoxy-2′-benzyloxy flavone (VIII) is methylated and subsequently debenzylated using acetic acid and hydrochloric acid. 3:7-Dimethoxy-2′-hydroxy flavone (X) obtained thereby undergoes para-nuclear oxidation with potassium persulphate yielding the quinol (XI) which, on methylation, yields 3:7:2′:5′-tetramethoxy flavone identical with the sample obtained by the direct flavone synthesis.

A study of the colour reactions of the new compounds is of interest. Compound (X) is the first example obtained so far having a free hydroxyl group only in the 2′-position. It does not give the ferric chloride colour thus ruling out the existence of chelation between the hydroxyl and the pyrone oxygen. A lone hydroxyl in the 8-position gives a prominent colour with alcoholic ferric chloride.[2] That given by a 5-hydroxyl which is chelated with the CO group is well known. Even the quinol (XI) is very unimpressive in its colour reactions as compared with primetin[3] (XII *a*) or 3-methoxy primetin[4] (XII *b*). It gives no colour with ferric chloride and with

alkali only a light yellow. Its oxidation with *p*-benzoquinone to give a red coloured product is very slow. The tetra- and penta-hydroxy flavones (VI *a*, VI *b*) do not give prominent colours in alkaline solution as is common with flavonols having the quinol unit in the condensed benzene ring (*e.g.*, 3-hydroxy primetin),[4] but they give red colour with excess of ferric chloride and benzoquinone. It is remarkable that these compounds and their derivatives do not give any detectable fluorescence. The 2′ : 5′ combination of hydroxyl and methoxyl groups seems to inhibit fluorescence emission.



EXPERIMENTAL

2: 5-*Dimethoxy benzoic acid*

2: 5-Dihydroxy benzoic acid required for this purpose was prepared in about 40% yield by the nuclear oxidation of salicylic acid with potassium persulphate in alkaline medium. If sodium persulphate is used in excess and the volume of the solution kept down as low as possible the yield of gentisic acid can be raised considerably (60 %). It crystallised from water as colourless needles melting at 200–01°. It gives a deep blue colour with alcoholic ferric chloride. Its methylation to dimethyl ether was carried out earlier by Mauthner.[5] The following method is more convenient and gives a good yield of a pure product.

Gentisic acid (5 g.) was refluxed in dry acetone (250 c.c.) solution with ignited potassium carbonate (25 g.) and freshly distilled dimethyl sulphate (17 c.c.) for a period of 50 hours. The acetone solution was filtered and the potassium salts washed with a small quantity of hot acetone. On distilling off the solvent from the filtrate a brownish yellow viscous oil was left which was taken in ether and washed twice with 2% cold aqueous sodium hydroxide to free it from any monomethyl ether. The oily mass obtained after the evaporation of ether was hydrolysed by refluxing it with 10% aqueous sodium hydroxide for 2 hours. The brownish red solution was filtered and acidified when the dimethyl ether of gentisic acid separated out as a pale brown solid. It crystallized from hot water as colourless needles melting at 76°; yield 5·1 g. It did not give any colour with alcoholic ferric chloride.

Anhydride of 2: 5-*Dimethoxy benzoic acid*

Dry 2: 5-Dimethoxy benzoic acid (20 g.) was taken in anhydrous ether (75 c.c.) in a 500 ml. conical flask and dry pyridine (8·6 c.c.) added to it. The contents were cooled to 0° C. and a solution of thionyl chloride (4 g.) in dry ether was slowly added in small lots with frequent shaking during the course of 30 minutes maintaining the temperature below zero during the addition. The flask was left in the refrigerator overnight, the solid mass filtered and triturated successively with ice-cold dilute hydrochloric acid, ice-cold 5% sodium bicarbonate solution and cold water. It was finally washed thoroughly with water to remove traces of sodium bicarbonate. The solid anhydride was dried by pressing between folds of filter-paper and keeping in a vacuum desiccator for a few days. The dry anhydride was crystallized from dry ethyl acetate and petroleum ether mixture when it appeared as colourless needles and rectangular prisms melting at 97–8° (Found: C, 62·9; H, 5·4. $C_{18}H_{18}O_7$ requires C, 62·4; H, 5·2%).

7-*Hydroxy*-3: 2′: 5′-*trimethoxy flavone* (*V a*)

ω-Methoxy resacetophenone (2 g.) was intimately mixed with gentisic anhydride (16 g.) and sodium gentisate (4 g.) and heated in an oil-bath at 180–85° for 4 hours under reduced pressure. The dark viscous mass thus obtained was left overnight and refluxed for 30 minutes with 7% alcoholic potash (5·3 g. in 80 c.c.). Most of the alcohol was removed by heating over a steam-bath under vacuum, the residue dissolved in water and the dark brown solution was filtered and saturated with carbon dioxide. It was extracted with ether, the ether extract dried over anhydrous sodium sulphate and the solvent distilled off. The reddish yellow mass thus obtained was crystallized from ethyl acetate-petroleum ether mixture. The compound came out in the form of pale yellow wedge-shaped crystals melting

at 240–42°; yield 1·8 g. (Found: C, 66·1, H, 5·1. $C_{18}H_{16}O_6$ requires C, 65·9; H, 4·9%). It did not develop any colour with alcoholic ferric chloride, gave a pale yellow solution with 5% sodium hydroxide and on reduction with magnesium and hydrochloric acid developed a red colour. With concentrated sulphuric acid it showed no fluorescence.

3:7:2′:5′-*Tetramethoxy flavone* (*VII a*)

The above 7-hydroxy compound (0·5 g.) was dissolved in anhydrous acetone (75 c.c.) and boiled with dimethyl sulphate (0·6 c.c.) and anhydrous potassium carbonate (6 g.) for 8 hours. The tetramethoxy flavone initially came out as a viscous oil which gradually solidified on cooling and scratching with a glass rod. It crystallized from ethyl acetate and petroleum ether mixture as colourless flat needles and rectangular rods melting at 169–70°; yield, 0·41 g. (Found: C, 66·9; H, 5·3. $C_{19}H_{18}O_6$ requires C, 66·7; H, 5·3%). It was insoluble in cold dilute sodium hydroxide, gave no colour with aqueous ferric chloride and on reduction with magnesium and hydrochloric acid developed a deep red colour. With concentrated sulphuric acid it exhibited no fluorescence.

3:7:2′:5′-*Tetrahydroxy flavone* (*VI a*)

7-Hydroxy-3:2′:5′-trimethoxy flavone (1 g.) was dissolved in acetic anhydride (20 c.c.) and to the solution was added hydriodic acid (10 c.c.; *d*, 1·7) cautiously with cooling. The solution was refluxed for 2 hours at 140°, diluted with sulphur dioxide water (100 c.c.) and left in the refrigerator overnight. The precipitated hydroxy-flavone was filtered off, washed thoroughly with sulphur dioxide water and finally with water. It was first crystallized from dilute alcohol and then from ethyl acetate-petroleum ether mixture when it came out as yellow tiny prisms melting at 270–71°; yield 0·4 g. (Found: C, 62·6; H, 3·9. $C_{15}H_{10}O_6$ requires C, 62·9; H, 3·6%). The tetrahydroxy flavone gave an olive-green colour with aqueous ferric chloride changing to red with excess of the reagent. With *p*-benzoquinone solution in alcohol it developed a dark red colour and it was soluble in aqueous bicarbonate and carbonate giving yellow solutions. With sodium hydroxide solution an orange-yellow colour was given and with concentrated sulphuric acid it exhibited no fluorescence.

5:7-*Dihydroxy*-3:2′:5′-*trimethoxy flavone* (*V b*)

A mixture of ω-methoxy phloroacetophenone (2 g.), 2:5-dimethoxy benzoic anhydride (18 g.) and sodium gentisate (4 g.) was maintained at 180–85° for 4 hours under reduced pressure and the product worked up as usual. The flavonol was first crystallized from alcohol and finally from

ethyl acetate-petroleum ether mixture when it appeared as yellow soft needles melting at 271–72°; yield, 1·9 g. (Found: C, 62·9; H, 5·1. $C_{18}H_{16}O_7$ requires C, 62·8; H, 4·7%). It gave a red colour with magnesium and hydrochloric acid and a brownish red colour with aqueous ferric chloride and did not emit any fluorescence with concentrated sulphuric acid.

3:5:7:2′:5′-*pentamethoxy flavone* (*VII c*)

The above trimethyl ether (0·5 g.) was methylated using anhydrous acetone (75 c.c.), dimethyl sulphate (1·5 c.c.) and potassium carbonate (5 g.) and refluxing on a water-bath for a period of 40 hours. The pentamethoxy flavone crystallized from acetone as colourless aggregates of rectangular plates melting at 142–43°; yield, 0·47 g. (Found: C, 64·1; H, 5·5. $C_{20}H_{20}O_7$ requires C, 64·5; H, 5·4%). It did not give any colour with aqueous ferric chloride, was insoluble in cold dilute sodium hydroxide and developed a red colour on treatment with magnesium and hydrochloric acid. With concentrated sulphuric acid it gave no fluorescence.

3:5:7:2′:5′-*Pentahydroxy flavone* (*VI b*)

The trimethoxy compound (V *b*) (1 g.) was refluxed with acetic anhydride (20 c.c.) and hydriodic acid (10 c.c., *d*, 1·7) for 2 hours at 140° and the product worked up as usual. The flavone was first crystallized from dilute alcohol and finally from ethyl acetate-petroleum ether mixture when beautiful yellow tiny prisms were obtained decomposing at 306–8°; yield 0·45 g. (Found: C, 59·8; H, 3·6. $C_{15}H_{10}O_7$ requires C, 59·6; H, 3·3%). It gave an olive-green colour with aqueous ferric chloride changing to cherry red on the addition of excess of the reagent. With *p*-benzoquinone solution in alcohol it developed a deep red colour. It was soluble in aqueous sodium bicarbonate, carbonate and sodium hydroxide giving in each case a yellow solution and did not give any fluorescence with concentrated sulphuric acid.

2-*Benzyloxy-benzoic anhydride*

2-Benzyloxy benzoic acid required for this preparation was made according to the procedure adopted by Cohen and Dudley.[6]

To a suspension of the dry acid (22·8 g.) in anhydrous ether (100 c.c.) containing anhydrous pyridine (4 c.c.) was added thionyl chloride (3·6 c.c.) little by little with shaking at 0° over a period of 45 minutes. After the addition of thionyl chloride, the flask was left in the refrigerator overnight, the semisolid mass was taken up in ether and the ether extract was washed respectively with cold dilute hydrochloric acid, cold aqueous sodium bicarbonate and finally with cold water. It was then dried and the solvent distilled off when the anhydride was left as a dark viscous mass. Further

drying was done by leaving it in a vacuum over sulphuric acid for two days; yield 16 g. The crude product had a boiling range of 255–60°/10 mm. and was directly employed for the condensation as such without purification by distillation. It was most convenient to use it as a solution in dry chloroform and distil off the solvent before the condensation.

7-Hydroxy-3-methoxy-2′-benzyloxy flavone (VIII)

An intimate mixture of ω-methoxy resacetophenone (3 g.) 2-benzyloxybenzoic anhydride (20 g.) and sodium 2-benzyloxy benzoate (6 g.) was heated under reduced pressure at 180–85° for 4 hours. The product was worked up as in similar cases. The crude product was obtained as a viscous oil which did not solidify on keeping in the refrigerator for several days. It was then taken up in ether, dried over magnesium sulphate and the solvent distilled off. Now the viscous mass partially solidified on leaving it for about ten days in the refrigerator. The solid was collected and crystallized from a mixture of ether and acetone when it appeared as colourless aggregates of beautiful tiny plates and flat needles melting at 195–96°; yield 1·2 g. (Found: C, 74·0; H, 4·5. $C_{23}H_{18}O_5$ requires C, 73·8; H, 4·8%). The substance gave no colour with aqueous ferric chloride, was soluble in aqueous sodium carbonate and sodium hydroxide and with concentrated sulphuric acid it gave a lemon yellow solution without any fluorescence.

3: 7-*Dimethoxy-2′-benzyloxy flavone (IX)*

The above compound (VIII) (0·9 g.) was methylated in dry acetone (100 c.c.) by refluxing for 8 hours with anhydrous potassium carbonate (5 g.) and dimethyl sulphate (0·4 c.c.). The dimethoxy flavone crystallized from dry ether in the form of colourless rectangular prisms melting at 116–17°; yield, 0·8 g. (Found: C, 74·3; H, 5·3. $C_{24}H_{20}O_5$ requires C, 74·2; H, 5·2%). It was insoluble in aqueous sodium carbonate and sodium hydroxide and gave no colour with ferric chloride. With concentrated sulphuric acid it exhibited no fluorescence.

3: 7-*Dimethoxy-2′-hydroxy flavone (X)*

3: 7-Dimethoxy-2′-benzyloxy flavone (0·8 g.) was dissolved in glacial acetic acid (18 c.c.) and concentrated hydrochloric acid (12 c.c.) added. The contents were heated over a water-bath for ninety minutes, diluted with water (150 c.c.) and left in the refrigerator for 4 hours. The solid was collected, dried and crystallized from ethyl acetate when it appeared as colourless rectangular plates melting at 190–91°; yield, 0·35 g. (Found: C, 68·6; H, 4·8. $C_{17}H_{14}O_5$ requires C, 68·4; H, 4·7%). It was soluble in aqueous sodium carbonate and sodium hydroxide giving in each case lemon yellow solutions and exhibited no fluorescence in concentrated sulphuric acid solution.

3: 7-*Dimethoxy-2′-5′-dihydroxy flavone* (*XI*)

To a stirred solution of the above flavone (X) (0·3 g.) in aqueous sodium hydroxide (0·35 g. in 10 c.c.) was added dropwise a saturated solution of potassium persulphate (0·8 g.) in the course of two hours, the temperature being kept between 15–20°. After 24 hours at room temperature the brown aqueous solution was neutralized with dilute hydrochloric acid to congo red, filtered and ether extracted. The aqueous layer was then acidified by the addition of further quantity of hydrochloric acid (10 c.c.) and the contents heated on a water-bath for 30 minutes when a brown solid slowly separated out. This was filtered, dried and crystallized from ethyl acetate when it came out as pale yellow rectangular rods and prisms melting at 237°; yield 0·08 g. (Found: C, 64·5; H, 4·7. $C_{17}H_{14}O_6$ requires C, 65·0; H, 4·5%). It developed no colour with alcoholic ferric chloride, was soluble in aqueous sodium carbonate and hydroxide giving lemon yellow solutions and with para-benzoquinone solution in alcohol it slowly developed a deep cherry red colour on keeping overnight. It did not exhibit fluorescence in concentrated sulphuric acid solution.

The dihydroxy compound (XI) was methylated using excess of dimethyl sulphate and anhydrous potassium carbonate in acetone medium. The tetramethoxy flavone (VII *a*) crystallized from a mixture of ethyl acetate and petroleum ether as colourless rectangular rods and flat needles melting at 169–70°. It did not give any colour with aqueous ferric chloride and was insoluble in aqueous alkali. The mixed melting point with the sample obtained from (V *a*) was not depressed.

SUMMARY

3: 7: 2′- 5′-Tetrahydroxy flavone and 3: 5: 7: 2′: 5′-pentahydroxy flavone and their derivatives are prepared and their colour reactions recorded. The flavone with only 2′-hydroxyl free (X) and also its 5′-hydroxyl derivative (XI) do not give any colour with ferric chloride indicating absence of chelation. Alkali colour reactions confirm the original finding that a quinol grouping in the side phenyl nucleus does not produce marked colour effects.

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SOME CONVERSE THEOREMS ON SUMMABILITY

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THE matrix $A \equiv (a_{ij})$ is called a Kojima or K-matrix if the following conditions are satisfied:—

(*a*) $\| A \| = \underset{1 \leqslant i < \infty}{\text{upper bound}} \sum_{j=1}^{\infty} | a_{ij} |$ is finite;

(*b*) $\lim_{i \to \infty} a_{ij} = \alpha_j$ exists for each fixed j;

(*c*) $\sum_{j=1}^{\infty} a_{ij} = \sigma_i$ converges to a limit as $i \to \infty$.

It is known† that the necessary and sufficient condition that $t_i = \sum_{j=1}^{\infty} a_{ij} s_j$‡ should converge to a limit as $i \to \infty$ whenever the sequence (s_j) converges is that $A \equiv (a_{ij})$ is a K-matrix.

The well-known class of Tauberian theorems, which assert the convergence of the sequence (s_j) from that of the transformed sequence (t_i), impose restrictions on the sequence (s_j) in relation to the matrix A. In this paper we seek conditions to be imposed on the matrix alone so that without any further restrictions on the sequence (s_j) than the minimum,‡ the convergence of (t_i) implies that of (s_j).

§2. The method used is to invert a K-matrix. For this purpose we first prove the

THEOREM 1. *The class Γ of K-matrices forms a Banach Algebra, with the usual definition of addition and multiplication and with the norm defined by* (*a*) *of* §1.

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* The author, Government of India Junior Research Scholar at Annamalai Uni ty, ack owledges with grateful pleasure the guidance and help received by him from Dr. V. Ganapathi Iyer regarding the results contained in this paper.

† For this and other properties of K-matrices, see *P. Dienes: Taylor Series*, Ch. XII, especially pp. 385 and 406–07.

‡ It is assumed that the series for each t_i converges.

Proof.—It is known that Γ forms a linear associative algebra. It is easily seen that $\| A \|$ defined by (*a*) of §1 is a norm on the elements of Γ and that if A, B are in Γ, then $\| AB \| \leqslant \| A \| . \| B \|$. So to complete the proof it is enough to prove the

THEOREM 2. *The space Γ is complete under the norm $\| A \|$.*

Proof.—Let $A^{(m)} = [a_{ij}^{(m)}]$ be a sequence of K-matrices. Then we have to show that

(1) $\| A^{(m)} - A^{(n)} \| \leqslant \epsilon$ for all $m, n \geqslant n_0$

is a necessary and sufficient condition that there should exist a K-matrix A such that

$$\| A^{(m)} - A \| \leqslant \epsilon \text{ for sufficiently large } m.$$

It is easily proved that the condition is necessary. To prove sufficiency, we have

(2) $\sum_{j=1}^{\infty} | a_{ij}^{(m)} - a_{ij}^{(n)} | \leqslant \epsilon$ if $m, n \geqslant n_0$ (n_0 independent of i).

Hence $a_{ij}^{(m)}$ tends to a limit a_{ij} as $m \to \infty$, for each fixed pair i and j. We shall show that the matrix $A = (a_{ij})$ is in Γ and that $A^{(m)} \to A$ in Γ.

Letting $m \to \infty$ in (2), we get

(3) $\sum_{j=1}^{\infty} | a_{ij} - a_{ij}^{(n)} | \leqslant \epsilon$ if $n \geqslant n_0$.

Also $\sum_{j=1}^{\infty} | a_{ij} - a_{ij}^{(n_0)} | \geqslant \sum_{j=1}^{\infty} | a_{ij} | - \sum_{j=1}^{\infty} | a_{ij}^{(n_0)} |$.

Hence by (3), $\sum_{j=1}^{\infty} | a_{ij} | \leqslant \sum_{j=1}^{\infty} | a_{ij}^{(n_0)} | + \epsilon$

and so is by (*a*) of §1 bounded independently of i. Writing $\sigma_i = \sum_{j=1}^{\infty} a_{ij}$, $\sigma_i^{(n)} = \sum_{j=1}^{\infty} a_{ij}^{(n)}$, etc., we have by (2), (3) and the property (*c*) of a K-matrix defined in §1,

$$\begin{aligned} | \sigma_i - \sigma_l | &\leqslant | \sigma_i - \sigma_i^{(n_0)} | + | \sigma_i^{(n_0)} - \sigma_l^{(n_0)} | + | \sigma_l^{(n_0)} - \sigma_l | \\ &\leqslant 3\epsilon \text{ if } i, l \geqslant l_0. \end{aligned}$$

So σ_i tends to a limit as $i \to \infty$.

Also, for a fixed j, $| a_{ij} - a_{lj} |$

$$\begin{aligned} &\leqslant | a_{ij} - a_{ij}^{(n_0)} | + | a_{ij}^{(n_0)} - a_{lj}^{(n_0)} | + | a_{lj}^{(n_0)} - a_{lj} | \\ &\leqslant 3\epsilon \text{ if } i, l \geqslant l_0. \end{aligned}$$

Hence $a_{ij} \to$ a limit as $i \to \infty$, for each fixed j.

From these results and (3), it follows that A is in Γ and that $A^{(m)} \to A$ in Γ. This proves Theorem 2 and therefore completes the proof of Theorem 1.*

§3. THEOREM 3.* *Let A be a K-matrix and λ any complex number such that* $|\lambda| < \frac{1}{\|A\|}$. *Then the matrix* $I - \lambda A$ *has an inverse which is itself a K-matrix.*

Proof.—Consider the infinite series $I + \lambda A + \lambda^2 A^2 + \ldots + \ldots$. The series will converge to a matrix $D \epsilon \Gamma$ if $\sum_{n=1}^{\infty} \| \lambda^n A^n \|$ converges, since Γ is complete. But $\| \lambda^n A^n \| \leqslant |\lambda|^n \cdot \| A \|^n$ and so the series will certainly converge if $|\lambda| < \frac{1}{\|A\|}$.

It is easily verified that $(I - \lambda A) D = D (I - \lambda A) = I$.

§4·0. The equation $A(BC) = (AB) C$ where A, B and C are infinite matrices is not in general true, but the equation holds good if A, B and C are triangular matrices or are row-bounded [the matrix A is said to be row-bounded when the condition (*a*) of §1 is satisfied], for in these cases, multiplication is associative. Now let the equations

$$y_i = \sum_{j=1}^{\infty} a_{ij} x_j \qquad (i = 1, 2, \ldots\ldots)$$

be represented as a matrix equation $y = Ax$, where x and y are column-matrices. If A is a K-matrix and by §3 has a K-matrix A^{-1} for its inverse, then the equations

$$A^{-1} y = A^{-1} (Ax) = (A^{-1} A) x = x$$

will be true, in particular, if *either* of the following conditions is satisfied:—

(i) *A is a triangular matrix.*—For then A^{-1} will also be a triangular matrix and x can also be considered as a triangular matrix by adding columns of zeros.

(ii) *The sequence* (x_i) *is bounded.*—That is, x is row-bounded; and A, A^{-1} being K-matrices and so row-bounded (but not necessarily triangular), multiplication is again associative.

* It has since been pointed out to the author that a similar result is proved in *R. G. Cooke:* "*Infinite Matrices and Sequence Spaces*," p. 30. Theorem 1, and Theorem 3 (which is true in any Banach Algebra) are proved here for the sake of completeness.

Theorem 3 now leads to the following converse theorems on summability.*

4·1. *Mercer's Theorem.*—If $y_n = x_n + \lambda \dfrac{x_1 + x_2 + \ldots + x_n}{n}$ converges and $|\lambda| < 1$, then the sequence (x_n) also converges. The matrix of transformation is of the form $I + \lambda A$ where A is the matrix associated with $(c, 1)$ summability and $\|A\| = 1$. Since condition (i) of §4·0 is satisfied, the result is seen to be true for $|\lambda| < 1$.

If we write $y_n = \alpha x_n + (1 - \alpha) \dfrac{x_1 + x_2 + \ldots + x_n}{n}$, it is known† that when $\alpha > 0$ and (y_n) converges then so does (x_n). The result in the previous paragraph does not give Mercer's theorem in its complete generality but shows that it is true when $R(\alpha) > \frac{1}{2}$.

4·2. THEOREM 4.‡ *Let* $y_n = x_n + a_1 x_{n-1} + \ldots + a_p x_{n-p}$ *tend to a limit as* $n \to \infty$, *where* p, $a_1, a_2, \ldots a_p$ *are fixed. Then the sequence* (x_n) *will converge if*

$$|a_1| + |a_2| + \ldots + |a_p| < 1.$$

Proof.—The matrix of transformation here is a triangular K-matrix of the form $I + A$ with $\|A\| < 1$. The result follows from Theorem 3.

4·3. The case $y_n = x_n + a_1 x_{n+1} + \ldots + a_p x_{n+p}$ can be reduced to the above by writing

$$v_n = x_{n+p}, \quad z_n = \frac{y_n}{a_p}. \quad \text{We get}$$

$$z_n = v_n + \frac{a_{p-1}}{a_p} v_{n-1} + \ldots + \frac{1}{a_p} v_{n-p}.$$

So if $$\left|\frac{a_{p-1}}{a_p}\right| + \left|\frac{a_{p-2}}{a_p}\right| + \ldots + \left|\frac{1}{a_p}\right| < 1,$$

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* These theorems which make use of the existence of inverses (of certain given K-matrices) in the Banach Algebra Γ' of K-matrices depend on the associative law for multiplication discussed above, being true. It is necessary to show that in each case multiplication is associative. In the original form of the manuscript the author overlooked this point and made some wrong assertions, *viz.*, the theorems in §5 without the hypothesis that the sequence (x_n) is bounded. The author is grateful to the referee for pointing out the mistake.

† See *Hardy: Divergent Series*, p. 104 for a proof of Mercer's theorem for $\alpha > 0$.

‡ The author thanks the referee for pointing out that this theorem has been proved in a more complete form by using the method of recurring series, by *Kubota*: *Tohoku Math. Journal*, 1917, **12**, 222–24. But the method of recurring series will not apply to a case like that disscussed in §4·4.

i.e., if $$1 + |a_1| + |a_2| + \ldots + |a_{p-1}| < |a_p|,$$

then (x_n) will converge whenever (y_n) converges for 4·0 (i) is satisfied.

4·4. As a slight generalisation consider the sequence (y_n) where

$$y_n = x_n + a_{n_1} x_{n-1} + \ldots + a_{np} x_{n-p}, \ (p \text{ fixed}).$$

If $$\text{upper bound}_{1 < n < \infty} \{|a_{n1}| + |a_{n2}| + \ldots + |a_{np}|\} < 1$$

and $$a_{n1} + a_{n2} + \ldots + a_{np} = \sigma_n \to \text{a limit as } n \to \infty,$$

then by §3 and §4·0, the convergence of (y_n) implies that of (x_n).

4·5. THEOREM 5. *Let $y_n = x_n + \lambda x_n'$ where x_n' is the rth. Cesaro mean of the sequence (x_n). Then if $|\lambda| < 1$, the convergence of (y_n) implies that of (x_n).*

For here the matrix is triangular and of the form $I + \lambda A$ where A is the matrix of the (c, r) process with $\|A\| = 1$. The result follows from §3 and §4·0.

§5·0. Let $y_n = x_n + \sum_{j=1}^{\infty} a_{nj} x_j$, where (a_{ij}) is a K-matrix with upper bound $\sum_{j=1}^{\infty} |a_{nj}| < 1$ for $1 \leqslant n < \infty$. If (x_n) is bounded and (y_n) is convergent, then (x_n) is convergent.*

The proof follows from the fact that the matrix of transformation is row-bounded, has a Kojima inverse by §3 and multiplication is associative by § 4·0 (ii).

§5·1. THEOREM 6. *Let $y_n = x_n + \lambda x_n'$, where x_n' is the Borel exponential mean $e^{-n} \sum_{k=1}^{\infty} n^k x_k / k!$ and $|\lambda| < 1$. Then if (y_n) converges, so does (x_n), if (x_n) is bounded.*

For Borel's exponential means is also a regular process the norm of whose matrix is unity and the result follows from §3 and §4·0 (ii).

5·2. Writing a K-matrix as an integral containing a parameter, we get the following theorem for Abel's summation process:

THEOREM 7. *If $A\left(\frac{1}{s}\right) + \lambda s \int_0^{\infty} e^{-st} A(t)\, dt$, [where the integrand is assumed to be summable in $(0, \infty)$ for all $s > 0$], tends to a limit as $s \to +0$,*

* If (x_n) is not bounded, the example $y_n = x_n - \frac{1}{2} x_{n+1}$, where $x_n = 2^n$ shows that the result is not true, as pointed out by the referee.

λ is a complex number with $|\lambda| < 1$ and $A(t)$ is bounded, then $A(t)$ tends to a limit as $t \to \infty$.

§6·0. It may very well happen that a transformation which is not a K-transformation, may yet have a K-transformation for its inverse. For example consider

$$y_n = a_n x_n - b_n x_{n-1} \qquad (n = 1, 2, 3, \ldots\ldots).$$

We write $\lambda_n = \dfrac{b_n}{a_n}$ and suppose that a_n and λ_n vanish for no value of n, and that $a_1 = 1$, $x_0 = 0$, and $\lambda_1 = 1$.

Solving for the x_n, we get

$$x_n = \frac{\lambda_2\lambda_3 \ldots . \lambda_n}{a_1} y_1 + \frac{\lambda_3 \ldots . \lambda_n}{a_2} y_2 + \ldots . + \frac{1}{a_n} y_n.$$

So the inverse transformation will be a K-transformation if

(1) $|\lambda_2\lambda_3 \ldots . \lambda_n| \left\{ \dfrac{1}{|a_1|} + \dfrac{1}{|\lambda_2 a_2|} + \ldots . + \dfrac{1}{|\lambda_2 \ldots . \lambda_n a_n|} \right\} < \infty,$

(2) $\lambda_2\lambda_3 \ldots . \lambda_n \left(\dfrac{1}{a_1} + \ldots . + \dfrac{1}{\lambda_2 \ldots . \lambda_n a_n} \right) = \sigma_n$ tends to a limit σ as $n \to \infty$, and

(3) $\dfrac{\lambda_i \lambda_{i+1} \ldots . \lambda_n}{a_{i-1}} \to$ a limit as $n \to \infty$ for each fixed i.

6·1. As an example we take Mercer's theorem.

Let $\quad y_n = x_n + \lambda \dfrac{x_1 + x_2 + \ldots . + x_n}{n} \quad (n = 1, 2, \ldots.), \lambda > -1.$

Put $\quad S_n = \dfrac{x_1 + x_2 + \ldots . + x_n}{n}.$

Then $\quad y_n = nS_n - (n-1) S_{n-1} + \lambda S_n$

$$= (n + \lambda) \left(S_n - \frac{n-1}{n+\lambda} S_{n-1} \right).$$

In the notation of §6·0 we now have $a_n = n + \lambda$; $\lambda_n = \dfrac{n-1}{n+\lambda} = 1 - \dfrac{\lambda+1}{n+\lambda}$.

We see that $\lambda_2\lambda_3 \ldots . \lambda_n \to 0$ as $n \to \infty$ and

$$\lambda_2\lambda_3 \ldots . \lambda_n \sim c \cdot e^{-\sum_{m=1}^{n} \frac{\lambda+1}{m+\lambda}} \sim c_1 e^{-(\lambda+1)\log n} = c_1 n^{-(\lambda+1)},$$

where c and c_1 are positive constants. Also $a_n = n + \lambda \sim n$ and it follows, since $n^{-(\lambda+1)} (1^\lambda + 2^\lambda + \ldots . + n^\lambda) \to \dfrac{1}{\lambda+1}$ as $n \to \infty$ when $\lambda + 1 > 0$,

that the conditions (1), (2) and (3) of §6·0 are satisfied. Hence Mercer's theorem is true for $\lambda > -1$ which corresponds to $\alpha > 0$ when the sequence for y_n is written as $y_n = \alpha x_n + (1-\alpha)\dfrac{x_1 + x_2 + \ldots + x_n}{n}$.*

6·2. In case the product $\lambda_2\lambda_3 \ldots \lambda_n$ of §6·0 either (i) converges to a limit $\neq 0$ or (ii) diverges to 0, as $n \to \infty$, then it is enough, as can be easily seen, that one more condition be satisfied, namely, that the series

$\sum_{i=1}^{\infty} \dfrac{1}{\lambda_1\lambda_2\lambda_3 \ldots \lambda_i a_i}$ converges absolutely.

Examples

(1) If $y_n = n^{\alpha}\left\{x_n - \left(1 - \dfrac{\lambda}{n^{\beta}}\right)x_{n-1}\right\}$, $(\alpha, \beta > 1)$, tends to a limit as $n \to \infty$, then so does the sequence (x_n).

In the notation of §6·0, we see that now $\lambda_2\lambda_3 \ldots \lambda_n \to l \neq 0$, as $n \to \infty$. It is enough to prove that $\sum_{i=1}^{\infty} \dfrac{1}{|\lambda_1 \lambda_2 \lambda_3 \ldots \lambda_i a_i|}$ converges. Since $\lambda_2\lambda_3 \ldots \lambda_n \to l$, it is sufficient if $\sum_{i=1}^{\infty} \dfrac{1}{|a_i|}$ converges, *i.e*, if $\sum_{n=1}^{\infty} \dfrac{1}{n^{\alpha}}$ converges, which it does since $\alpha > 1$. Hence the result.

(2) If in the above example we take $\beta = 1$, then $\lambda_1\lambda_2 \ldots \lambda_n \to 0$. Moreover $\lambda_1\lambda_2 \ldots \lambda_n \sim ce^{-\lambda \log n} = cn^{-\lambda}$; $a_n = n^{\alpha}$. So the series $\sum_{i=1}^{\infty} \dfrac{1}{|\lambda_1\lambda_2 \ldots \lambda_i a_i|}$ will converge if $\sum_{n=1}^{\infty} \dfrac{1}{n^{\alpha-\lambda}}$ converges, the condition for which is that $\alpha > 1 + \lambda$. When $\alpha > 1 + \lambda$, if $y_n = n^{\alpha}\left\{x_n - \left(1 - \dfrac{\lambda}{n}\right)x_{n-1}\right\}$ converges, then so does the sequence (x_n).

* This is substantially the same proof as in *Hardy, l.c.*

ANALYSIS OF AMINO ACIDS USING PAPER CHROMATOGRAPHY (HORIZONTAL MIGRATION)

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Analysing the amino acids using the horizontal migration method of paper chromatography, Giri has recently reported that " In general the values (Circular R_F values) are found to vary slightly from those reported by other workers by descending and ascending paper chromatographic techniques ".[1] This is however contrary to our experience with the analysis of sugars and uronic acids,[2, 3] wherein the variation between the circular and the straight R_F values has been not slight but considerable. Giri has not given any comparative data in support of his statement but a search into the literature shows that the values reported by Giri are very much different in several cases from the straight R_F values recorded by other workers (comparative data given in Table I), his figures being in some cases as high as 300 per cent. over the straight R_F values. We have, therefore, re-examined the whole problem, but we could not reproduce some of the analytical values reported by Giri nor could we substantiate his conclusion. The values now obtained are quite characteristic and reproducible, and are much different from the straight R_F values, and so this method may offer a convenient, quick and facile way of identifying the amino acids. As in the case of sugars the identification has to be confirmed by carrying out the experiment with two or more solvents.

The method followed is the same as the one already described in our earlier publications.[2, 3] Of the solvents tried, moist phenol, saturated either with water or salt solution, is not at all suitable for the irrigation, since the rings obtained are highly diffused and often leave a trail; further, some of the amino acids like cystine and serine get decomposed on coming into contact with phenol. The other solvents are as a class suitable, though in some cases there is diffusion even with them. It may be worthwhile to note that, as a rule, the values obtained with the three-component solvents are much higher than those obtained with the two-component solvents. In the preparation of these solvents, particularly the three-component systems, it is found necessary to keep the components, taken in measured quantities, together for a long time, preferably overnight, to attain perfect equilibrium conditions. Further, in the case of the three-component solvents, it is

essential to start with fresh amount for every irrigation, because even slight changes in the relative proportion of the components affect the R_F values appreciably.

Experimental

The experiments were conducted using Whatman No. 1 circular filter-papers (15 cm. in diameter). The provision of a detachable "tail" or "wick" for irrigating the filter-paper with the solvent, as suggested by Giri,[1, 4] was not found to be of any special advantage, and so the fixed tail technique as described by Rao and Beri[2] was followed. The tail was formed by making two parallel cuts perpendicular to the diameter and at equal distance from the centre, cutting off the piece lying between the two parallel cuts, at the ends away from the diameter, and folding it back, so that it is rectangularly perpendicular to the plane of the filter-paper. The length of the tail was cut down to about 1 cm. The amino acid solution (1 per cent. strong) was introduced with the help of a capillary tube as a microdrop at the centre of the filter-paper and air-dried. Taking the solvent into a small dish placed at the centre of a Petri dish (about 14 cm. in diameter), the filter-paper was placed over the Petri dish in the usual way, so that the tail dipped into the solvent below. It was then covered completely by a glass plate and the whole set-up was encaged by an inverted bigger Petri dish. The experiments were conducted in a thermostat maintained at 35° C.

When the irrigation was over (30 to 60 minutes depending on the nature of the solvent), the filter-paper was removed, the position of the solvent front marked and dried in an air-oven at 105° for about 5 minutes. It was then rapidly and evenly sprayed with ninhydrin solution in *n*-butanol (0·1 per cent. in strength) and dried again at 105°. Revealing the positions taken up by the amino acids, characteristically-coloured rings appeared in about two minutes. Their shades varied from bluish to reddish purple, excepting in the case of proline which produced a yellow ring. In a few cases there was a greyish tinge also. It may be noted in this connection that tryptophane was reported to give a blue colour[5] but in our experiments even this acid gave only a bluish purple ring. It should also be noted that the shades produced were to some extent dependent on the nature of the solvent used for the chromatogram. For instance, arginine and norvaline gave a bluish purple ring when moist collidine had been used for the irrigation, while they produced a reddish purple, when *n*-butanol-acetic acid-water was the irrigating medium. In general, the tinges produced with collidine as solvent were bordering on the bluish side. By noting down the distances traversed by the amino acid on the one hand and the solvent on the other, the circular R_F values were calculated in the usual way.

In his article Giri did not mention the temperature at which the R_F values were determined. Presuming that the work might have been done during the months of July, August and September, when the average day temperature of Bangalore would be about 25° C., the circular R_F values were determined at the same temperature using *n*-butanol-acetic acid-water (4 : 1 : 5 by volume; upper layer) and the following figures (Table I) were obtained. The values as recorded by Giri[1] and also the straight R_F values as determined by other workers[6, 7] are included in the table for the sake of comparison. From the results it would be clear that the circular R_F values differed considerably from the straight R_F values.

TABLE I

Circular R_F Values with Butanol-Acetic Acid-Water as Solvent

	Circular R_F values		Straight R_F values		
			Ascending method		Descending method
	The authors (25° C.)	Giri[1] (presumably 25° C.)	Burma[7]	Govindarajan and Sreenivasaya[6]	Woiwood (cited by Govindarajan & Sreenivasaya[6])
Alanine ..	0·58	0·44	0·25	0·35	0·32
Arginine ..	0·51	0·32	0·14	0·14	0·11
Asparagine ..	0·44	0·31	0·11	..	..
Aspartic acid ..	0·48	0·37	0·16	0·19	0·14
Cystine ..	0·60; 0·41	..	0·07	0·08	0·03
Glutamic acid ..	0·49	0·44	0·21	0·26	0·25
Glycine ..	0·48	0·37	0·18	0·20	0·19
Histidine, HCl* ..	0·52	0·50	0·13	0·11	0·11
Isoleucine ..	0·88; 0·58	0·70	0·61	..	0·65
Leucine ..	0·75	0·73	0·62	0·66	0·85
Lysine, HCl* ..	0·48	0·45	0·11	0·12	0·11
Methionine ..	0·65	0·92	0·43	0·48	0·82
Norleucine ..	0·79	0·75	0·68	..	..
Norvaline ..	0·72	..	0·52	..	..
Ornithine, HBr* ..	0·49	0·25	..	..	..
Phenylalanine ..	0·74	0·70–0·75	0·60	0·60	0·76
Proline ..	0·60	0·49	..	0·40	0·40
Serine ..	0·51	0·40	0·18	0·19	0·19
Threonine ..	0·59	0·44	0·21	..	0·25
Tryptophane ..	0·69	0·70	0·50	0·53	..
Tyrosine ..	0·62	0·58	0·41	..	0·53
Valine ..	0·65	0·62	0·47	0·47	0·62

* The hydrogen halide present in the salt does not interfere with the R_F value of the amino acid.

As reported earlier,[2] since for Indian laboratories 35° C. is a convenient temperature which could be maintained by means of a oven without resorting

TABLE II

Circular R_F Values of the Amino Acids at 35° C.

	Phenol saturated with salt solution		Moist *s*-collidine	Moist *n*-butanol		Moist *ter.* amyl alcohol		Butanol-acetic acid-water (4:1:5 by vol.)		Ethyl acetate-pyridine-water (2:1:2 by vol.)		Ethyl acetate-acetic acid-water (3:1:3 by vol.)	
	R_F values	Remarks	R_F values	R_F values	Remarks	R_F values	Remarks	R_F values	Remarks	R_F values	Remarks	R_F values	Remarks
Alanine	0·76	Diffused	0·21	0·27		0·10	Diffusion	0·57		0·21		0·42	
Arginine	..	do	0·12	0·18	Diffusion	..	Very little movement	0·53		0·12		0·19	
Asparagine	0·64	do	0·10	0·15		..	do	0·54	Two over lapping rings, one blue and one purple	0·33		0·28	
Aspartic acid	0·18	do	0·11	..	Very little movement	..	do	0·54		0·24	A 2nd ring at 0·18	0·31	
Cystine	..	No ring	0·11	0·07		..	No movement	0·60		0·08		0·16	
Glutamic acid	0·18	Diffused	0·12	..	Too much diffusion	..	do	0·56		0·21		0·35	
Glycine	0·45	do	0·15	0·23		..	do	0·55		0·34	Wide ring	0·35	
Histidine, HCl	..	do	0·18	0·21	Diffusion	..	do	0·53		0·25		0·18	
Isoleucine	..	do	0·41	0·54		..	Too much diffusion	0·85	A 2nd ring at 0·61 (yellow)	0·42		0·79	
Leucine	0·90	do	0·36	0·48		0·20		0·82		0·64		0·82	Diffusion
Lysine, HCl	0·72	do	0·13	.	Very little movement	..	No movement	0·51	Broad	0·16	Wide ring	0·15	
Methionine	0·82	do	0·36	0·44		0·22		0·72	A 2nd ring at 0·61 (faint)	0·61		0·67	
Norleucine	0·86		0·40	0·60		0·36		0·81		0·62		0·74	Diffusion
Norvaline	..	Diffused	0·34	0·52	Diffusion	..	Too much diffusion	0·72	A 2nd ring at 0·61 (faint)	0·36		0·61	
Ornithine, HBr	..	do	0·14	0·13	Diffusion	..	No movement	0·51		0·16	Diffusion	0·19	A 2nd ring at 0·05
Phenylalanine	..	do	0·40	0·55		0·32		0·75		0·62		0·69	Diffusion
Proline	..	do	0·23	0·31	A 2nd ring at 0·24 (faint)	0·11		0·61		0·25		0·52	
Serine	..	No ring	0·18	0·20		..	Very little movement	0·57		0·31	Wide ring	0·29	Diffusion
Threonine	0·69		0·19	0·26		0·08		0·57		0·37		0·33	
Tryptophane	.	Diffused	0·41	0·48		0·22		0·71		0·62		0·66	Diffusion
Tyrosine	..	do	0·34	0·33		0·16		0·62		0·62		0·60	
Valine	0·81	do	0·28	0·39		0·16		0·70		0·48	Wide ring	0·61	

to low-temperature incubators, the values were determined at this temperature with the commonly-employed solvents (Table II). It was noticed that in some cases (samples supplied by British Drug House, Ltd., Bombay) more than one ring was obtained. This was probably due to the presence of minute quantities of impurities rather than to any changes taking place during the course of the experiment. In such cases the more prominent ring was taken to represent the substance used. It was also noticed that in some cases, where somewhat broad rings were obtained, the edges were more intensely coloured than the intervening portion and this feature became more pronounced after 2 or 3 days, the central portion fading away more rapidly than the rest. This change was so prominent that in some cases one might mistake the edges to be two different rings. One guiding factor to avoid this mistake was that the edges and the central portion, if they are of the same ring, differed only in intensity. If there were two different rings, the portion in between should be almost colourless.

SUMMARY

Using the horizontal migration method of paper chromatography the separation and identification of naturally-occurring amino acids have been effected.

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SOUND VELOCITIES IN SOME INDIAN ROCK SPECIMENS

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1. Introduction

The determination of sound velocities and a study of related properties such as the elastic behaviour for rock specimens is of some importance to geologists and physicists. Adams and his collaborators and Bridgman (1931), Zisman (1933), Roess (1935) and a number of others employed static methods for studying the elastic behaviour of rocks. Birch and his collaborators (1936, '38, '39, '40 and 43) and Ide (1935, '36) and a few others studied the same problem by dynamic methods. Application of more recent techniques developed in the field of ultrasonics to such investigations has now been recognised as a fruitful branch of work and Schæfer (1942), Prasadarao (1947) and Bacher (1949) published a few results. Prasadarao's investigations on Indian rocks were of a preliminary nature as they did not include the determination of velocities of transverse ultrasonic waves nor did he correlate his results with certain important geological features such as the granular structure and variations in mineralogical composition from grain to grain in the specimen. Bacher, however, used ultrasonic methods to obtain the velocities of both longitudinal and transverse waves in certain rocks. The ultrasonic technique has, in recent years, been very much improved and it is thought desirable to make a detailed and more complete study, than has hitherto been done, of the specimens of Indian rocks. In this work, the ultrasonic wedge method developed by Bhagavantam and Bhimasenachar (1944) has been employed and over a dozen rock sections studied. In six cases, velocities of transverse waves also have been measured in addition to those of the usual longitudinal ones and some interesting observations made for the first time.

2. Descriptions of Rock Specimens

A brief description of the various rocks studied in these investigations is given below:

(*a*) *Sedimentary Rocks*

Limestone.—The colour is steel black. It is cryptocrystalline, equigranular, and no variation in chemical composition from grain to grain is noticed.

Grey Hyderabad Marble.—This Pakhal marble having a vitreous lustre is white in colour and equigranular. Calcite and other impurities are present in minute quantities.

Pink Rajputana Marble—The fine-grained pink marble has a pearly lustre and is equigranular. No variation in chemical composition is noticed.

Shale.—When welded into a compact rock, argilaceous material is called s hale.

(*b*) *Igneous Rocks.*

Pink Hyderabad Granite.—The colour is mottled pink, white and black due to felspars and biotite respectively. The texture is inequigranular and variation in chemical composition from grain to grain is seen.

Deccan Trap.—This rock is dark in colour, black to greyish-black on fresh fractured surfaces. The texture is more or less equigranular. Labrodorite and Enstatite augite are the essential constituents. There is a uniformity in chemical composition and in structural features as has been pointed out by Krishnan (1949).

Dolerite (*Hyderabad*).—It is a green rock essentially composed of felspar, chlorite and augite. It is very much altered and inequigranular in texture.

Gneiss.—The crystals of hornblende are linearly arranged. Interwoven with these bands, there are elongated prisms of zoisite. Quartz is present in abundance. The gneissic texture is clear and the rock is equigranular.

3. EXPERIMENTAL RESULTS

In the following tables are given the results obtained in the present investigation. All the moduli are in units of 10^{11} dynes/cm.^{2} In these tables, d = thickness of section in mm.; ρ = density in gm./c.c.; v_1 = longitudinal velocity in m./sec. ; v_t = torsional velocity in m./ sec.; c_{11}= effective longitudinal elastic constant; c_{44}= effective torsional elastic constant; Y = Young's modulus; n = modulus or rigidity and K = Bulk modulus.

Tables I and II respresent broadly two classes of rock sections. Figs. (*a*) and (*b*) in Pl. XVI show the transmission patterns obtained from limestone (1) and Deccan Trap (3) respectively, both chosen from the group contained

TABLE I

No.	Rock	d	ρ	v_1	v_t	c_{11}	c_{44}	Y	n	K
1	Limestone (Pidiguralla area)	2·57	2·84	6362	3084	11·5	2·7	7·3	2·7	7·9
2	Limestone (Bhima)	1·52	3·00	6212	3100	11·6	2·9	7·7	2·9	7·7
3	Deccan Trap (Gulbarga)	1·95	3·10	6477	4095	13·0	5·2	12·1	5·2	6·1
4	Do	3·20	3·10	6463	4096	13·0	5·2	12·1	5·2	6·1
5	Hyderabad Marble	1·85	2·88	6832	3811	13·5	4·2	10·7	4·2	7·9
6	Rajputana Marble	1·65	2·93	5611	3465	9·2	3·5	8·3	3·5	4·5

TABLE II

No.	Rock	d	ρ	v_1	c_{11}
1	Dolerite ..	2·32	3·12	5146	8·2
2	Shale ..	1·48	3·07	4934	7·5
3	Granite (pink) .	1·90	2·74	6396	11·2
4	Granite (grey) ..	1·86	2·82	6407	11·6
5	Granite (green) ..	1·91	2·76	7078	13·8
6	Gneiss ..	3·35	2·83	6766	13·0

in Table I. Similarly Figs. (*c*) and (*d*) are the patterns obtained from pink granite and gneiss chosen from the group in Table II. The comparatively feeble transmission and the consequent presence of only one prominent order of diffraction on either side of the centre in the latter cases is a noteworthy feature of the pictures. Care has been taken to use nearly the same thickness and maintain the same oscillator power in all the above cases. In spite of special efforts, transverse oscillations could not be excited in the group of rocks described in Table II.

In certain cases, where doubts have arisen as to the correctness of the fundamental frequency of the rock section chosen, either by its being too close to one of the natural frequencies of the oscillating crystal or by other inherent difficulties in interpretation when it gets mixed up with the spurious maxima exhibited by the wedge, further work has been done by preparing sections with different thicknesses from the same rock and verifying that the fundamental frequency varies inversely with the thickness.

4. SOME SPECIAL FEATURES OF THE INVESTIGATION

A complete determination of elastic constants in rocks, which are in the nature of polycrystalline aggregates, presents special difficulties. The elastic properties of aggregates are dependent on the randomness of arrangement, closeness of packing, particle size and mineralogical composition of the crystallites on granules composing the aggregates. Some of these aspects have been mentioned by Birch and Bancroft in their earlier work on rocks (1939). If the crystallites are distributed in a perfectly random manner in space, the problem becomes somewhat simpler and the resulting polycrystalline aggregate will be elastically isotropic. It will then exhibit only two elastic constants. For simplicity, rock sections under investigation, are chosen in random direction and since they are generally small, the large-scale structural variations in the rock get eliminated from the problem. Nevertheless the finer or grain to grain variations of size and mineralotical composition continue to be of considerable significance as will be seen later. Mention may be made of one other complication which arises in such studies and that is the presence of minute foreign matter usually occurring in the form of cementing material between various granules.

On account of these special features in the case of rocks, it was found difficult to determine c_{44} which is the torsion constant by the wedge method. This is undoubtedly to be interpreted by saying that in a composite material like a rock it is not so easy to excite torsional waves as in a metal or a crystal plate. Instead of a wedge, quartz plates of other cuts such as AT, BT and Y have also been tried with a view to see if the rock section could be forced to oscillate at places where there is no regular resonance but without success.

Finally, after several trials, a Y-cut plate having a thickness of 1·5 mm. and an area, comparatively much smaller than that of the rock section, had to be chosen and cemented to the rock section for the purpose of successfully exciting torsions. In this set-up it was found that the shear modes are excited more prominently than the longitudinal ones. From the transmission maxima, the shear modes are easily sorted out and the corresponding fundamental frequency calculated.

It must be remarked here that if the rock section and the oscillating crystal stuck on the section have comparable dimensions, they have been found to constitute themselves into a composite system and complicated modes are excited, making it difficult to get at any of the natural frequencies of the rock or of the crystal.

5. DISCUSSION OF RESULTS

One outstanding result of the present investigation is that strong ultrasonic patterns showing a large number of diffraction orders are shown by

one set of rocks (Figs. *a* and *b*), whereas the other set shows comparatively feeble transmission (Figs. *c* and *d*). Broadly speaking, all the rocks classified in Table I are of the first category and their geological structure is such that there are no violent variations of mineral composition from grain to grain in them. On the other hand, the rocks classified in Table II are characterised by an inequigranular structure. Granites, for instance, contain several types of grains such as quartz, felspar and mica. These differences manifest themselves in sound transmission and enable us to divide them broadly into two classes. In rocks where the structure is markedly inequigranular, sound absorption takes place to a large extent, probably by a process of scattering. In rocks where the granular structure is more uniform and where chemical composition does not vary from grain to grain, it has generally been found that there is a free transmission of ultrasonic waves. Further it has been observed that in the whole group of rocks, given in Table II, it was not possible to excite torsions even with the special methods employed for obtaining them in the group given in Table I. These results suggest that sound transmission depends upon the particle size, the closeness of packing and the variation in chemical or mineralogical composition from grain to grain. Only in rocks, where all these conditions are prevalent in a reasonably uniform manner from place to place, it is possible to get definite and intense sound transmission maxima. A further distinction of interest has been found between rock sections and metal or single crystal plates in that in the former the transmission maxima are generally not sharp as in the case of latter materials.

The author's values for longitudinal velocity and the effective longitudinal elastic constant are in general agreement with those of Prasadarao (1947) who also worked with Indian rocks. In Table III, the values for v_1 and v_t obtained in the present investigation are compared with those of Bacher who worked with similar rocks though they belong to a different geological formation in another part of the world. The agreement is fairly good.

TABLE III

Observer	Limestone		Marble		Gneiss		Basalt	
	v_1	v_t	v_1	v_t	v_1	v_t	v_1	v_t
Bacher ..	6130	3200	6150	3260	7870	3010	5930	3140
Author ..	6212	3100	6832	3811	6766	..	6477	4095

6. SUMMARY AND CONCLUSION

The paper gives the elastic moduli and other relevant features obtained from measurements on sound velocities in about a dozen specimens of Indian rocks.

This systematic investigation of the ultrasonic sound velocities (longitudinal and torsional) in various rock sections by the wedge method, has shown that the differences in granular structure and mineralogical composition from grain to grain are reflected in the transmission patterns that are obtained. Typical cases like limestone, consisting of practically the same chemical substance all through the section, give intense ultrasonic patterns with a large number of diffraction orders. In these rocks we are enabled, by special techniques, to determine both longitudinal and torsional velocities. Cases like granite, on the other hand, consisting of a variety of materials like mica, felspar and quartz give weak ultrasonic patterns and appear to scatter the sound to a large extent. Torsions are not easy to excite in these cases.

There is a further point of interest that in these rocks, the transmission maxima are fairly broad unlike what we get in metals and single crystal plates where they are generally sharp.

In conclusion, the author desires to express his grateful thanks to Dr. S. Bhagavantam for providing the necessary facilities for this work in the Physical Laboratories at the Osmania University.

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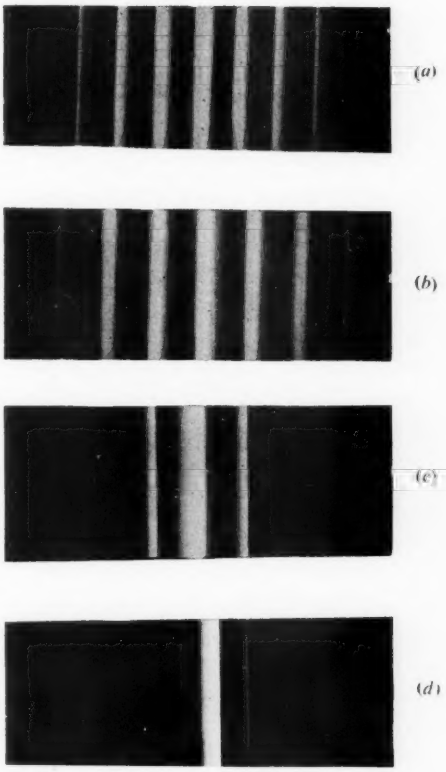

Ultrasonic diffraction patterns through Rock Sections

AGING OF SURFACES OF INVERTASE SOLUTIONS

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Received July 2, 1952

(Communicated by Dr. K. S. G. Doss, F.A.SC.)

Introduction

The spreading properties of invertase have been reported in a former paper.[1] In view of the magnitude of spreading being known, it is of special interest to study the accumulation of invertase at the surface of its aqueous solution. In the present work are presented the results obtained with invertase solutions on (*a*) change of surface tension with time and (*b*) the rate of accumulation at different pH.

Experimental

Apparatus Used.—The film balance used has been described previously.[2] The trough was made by fixing glass strips on glass plate by paraffin wax. The apparatus was enclosed in a glass cabinet to avoid contamination of substrata.

Materials Used.—The sample of invertase used was supplied by Messrs. Sugar Manufacturers' Supply Co., Ltd., 7-8, Idol Lane, London. As per details kindly supplied by the firm, the invertase was prepared from Baker's yeast, carefully purified and stabilised by using purest glycerine and has been certified as not containing any other surface-active substance or nitrogenous substance. The nitrogen content of the sample was found to be $0{\cdot}65 \pm 0{\cdot}06$ mg./c.c. The time value of the invertase sample was 58 minutes.

Other chemicals used were of C.P. quality.

Results

1. *Variation of Surface Tension with Time.*—The variation of surface tension of invertase solutions was studied by the method already described.[3] The reference surface used in the trough was one-minute old.

The stock solution was examined for its activity. 1·0 c.c. of the concentrated invertase solution in 25 c.c. of the inverting mixture (as per

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standard procedure for determining the time value) gave a time value of 58 minutes. The stock solution diluted 83·3 times by volume has been designated as having concentration C. The other solutions which are more dilute are designated C/2, C/4, etc., according to the extent of dilution.

Sufficient quantity of hydrochloric acid was added during dilution so as to get the desired pH. The results are given in Fig. 1.

2. *Rate of Accumulation.*—The method of measuring the rate of accumulation is the same as described previously.[4] The areas of the film were measured at a pressure of 2 dynes/cm. against a one-minute old reference surface. It was found however, that owing to high dilutions being worked with, considerable change in concentration occurred during even a single

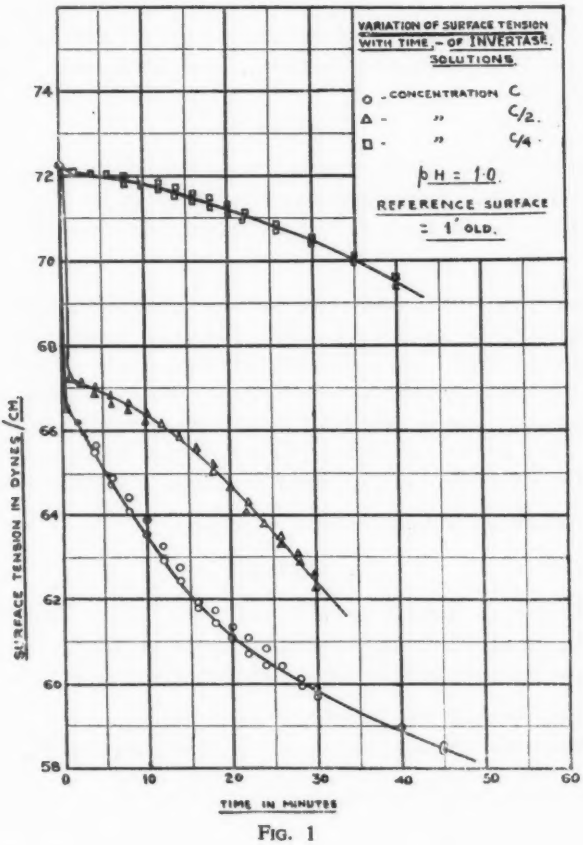

FIG. 1

accumulation at pH 1·0. This resulted in the successive accumulation rates becoming progressively lower. This can be seen from the one-minute values for accumulation taken successively a number of times from the same solution in the trough at pH 1·0, illustrated in Fig. 2. To minimise error

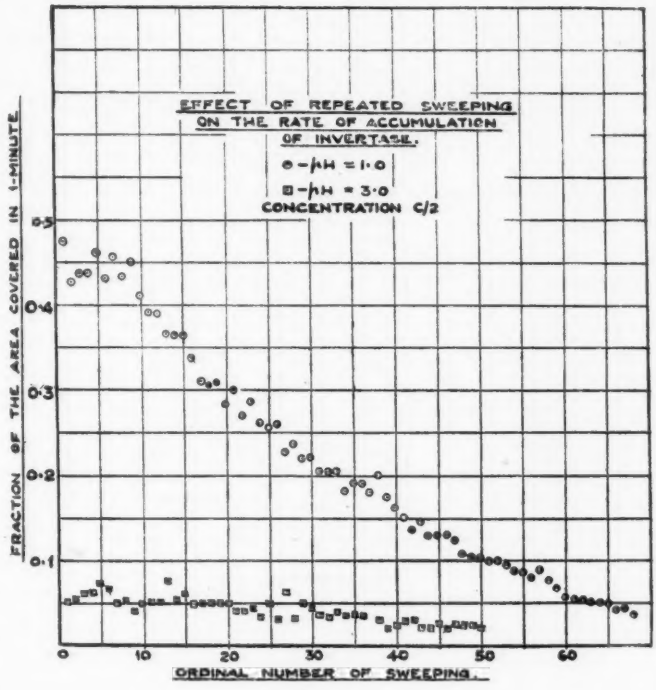

FIG. 2

from denudation in later experiments fresh solution was employed invariably for each value of accumulation. At pH 3·0, however, the denudation is not marked. The time-area curve is given in Fig. 3.

The effect of 10% ammonium sulphate on the rate of accumulation was studied at pH 3·0 and it was found that the rate of accumulation is slightly enhanced as shown in Fig. 3.

Accumulation of Formalised Invertase.—Formalised invertase was prepared by mixing solution of invertase with formaldehyde and allowing it to stand for 48 hours. The rate of accumulation of C/2 concentration in 0·1 M hydrochloric acid was studied. The results are given in Fig. 3.

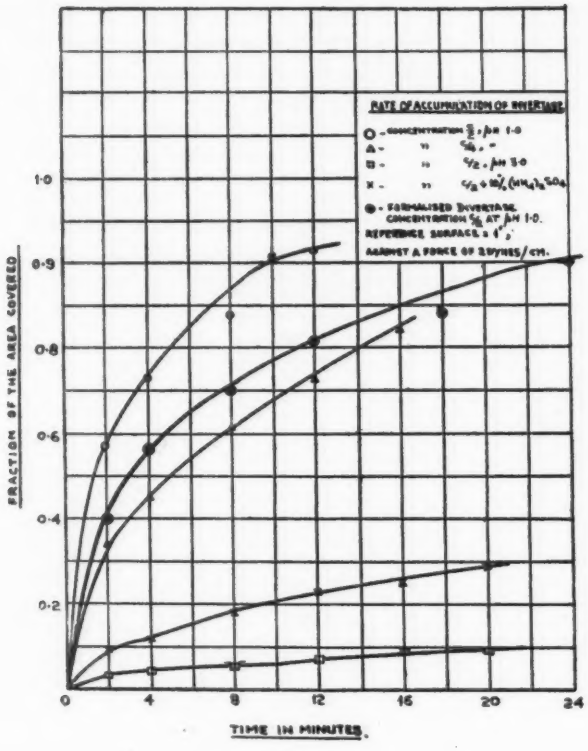

FIG. 3

DISCUSSION

1. *Variation of Surface Tension with Time.*—The form of surface tension-time curve happens to be different from any of the curves met with so far such as thymol blue, bromothymol blue, bromophenol blue and casein. The surface tension falls steeply first; this is followed by a slow fall which in its turn is followed by a steep fall. Finally the rate of fall becomes slow and the curve tends to become asymptotic parallel to X-axis. These features can be interpreted in terms of the known facts of invertase. It is known that invertase contains two fractions having the molecular weights of 3,500 and 1,00,000 respectively. The first steep fall appears to be due to the low molecular weight fraction accumulating very fast and bring about the first steep fall in surface tension. The heavy molecules however form condensed film practically as a separate phase and so do not contribute towards the surface pressure to any high degree. When, however, the surface gets

nearly full further penetration of the solute molecules would change the surface pressure markedly thereby bringing about comparatively quick change of surface tension. In the next stage when the surface is practically full further accumulation slows down considerably and thereby the curve tends to become parallel to X-axis.

2. *Denudation Due to Accumulation.*—It was found that at pH 1·0 the accumulation rate is quite large. Since the solutions are dilute, considerable changes in concentration take place even by a single sweeping. This can be seen from Fig. 2 wherein are shown the successive one-minute values obtained from the same invertase solution in the trough. At pH 3·0 however the accumulation is much slower and hence the denudation is also marked as can be seen from Fig. 2. This type of denudation has also been noticed in the case of casein.[5]

3. *Rate of Accumulation of Invertase.*—It is found that rate of accumulation is quite high at pH 1·0 but gets tremendously lowered at pH 3·0. Addition of 10% ammonium sulphate at pH 3·0 appreciably enhanced the rate of accumulation. It is also seen that formalised invertase accumulates slower than the original invertase at pH 1·0. The low accumulation at pH 3·0 is perhaps due to invertase getting strongly hydrophilic at this pH. This is supported by the fact that spreading of invertase is considerably lowered at this pH. This has been shown by special technique developed in this laboratory as due to the molecules mostly getting in the interior during spreading process.

The data on variation of surface tension with time also support this view. It is found that the surface tension hardly falls by 0·08 dyne even after 30 minutes, at pH 3·0, showing thereby that the molecules are highly hydrophilic.

Formalisation itself may bring about aggregation of invertase molecules making accumulation slower.

4. *Determination of the Dimension of Invertase Molecule.*—This system is of unique interest since it is possible to get films of this substance by spreading as well as by accumulation. This enables us to estimate the order of dimension of the invertase molecules. There is complication no doubt due to the fact that we are dealing with a mixture. Nevertheless it will be attempted to calculate the order of dimension of the molecules composing the lighter fraction of invertase. For this calculation it will be assumed that there is no potential barrier for the accumulation process. The accumulation can be pictured as taking place by Brownian displacement of the molecules. If a depth equal to Δ from the surface would be denuded

in t seconds, half the number of molecules going to the surface and the other half going to the interior, then Δ is given by the equation

$$\frac{\Delta^2}{t} = \frac{RT}{N}\frac{1}{3\pi\eta r} \qquad (1)$$

Let us calculate Δ from the experimental data. Consider the accumulation at a 1 sq. cm. of the surface in 120 seconds. A fraction 0·575 of the total surface gets covered by the accumulated invertase as measured at a surface pressure of 6·7 dynes/cm. But it is known[1] that invertase contained in 0·06 c.c. of original solution or 10 c.c. of the present dilute solution used for accumulation when spread would occupy 533 sq. cm. at a surface pressure of 6·7 dynes/cm. Thus to get 0·575 sq. cm. to be covered by invertase it would be necessary to denude $\frac{10}{533} \times 0{\cdot}575 \times 2$ c.c. of the solution. This gives value of Δ in cm. which comes out to be 0·0216 cm.

From equation (1) we get

$$r = \frac{RT}{N} \cdot \frac{1}{3\pi\eta} \cdot \frac{t}{\Delta^2}$$

Substituting the values

$R = 8{\cdot}32$ .. .. $\eta = 0{\cdot}01$

$T = 300$ .. .. $t = 120$ secs.

$N = 6{\cdot}1 \times 10^{23}$ .. .. $\Delta = 0{\cdot}0216$ cm.

we get $r = 1{\cdot}1 \times 10^{-7}$ cm. which is the equivalent diffusion radius of the accumulating invertase molecules. It would be of interest to determine the dimension of the invertase molecule by other methods and compare with this value. The low value indicates that mostly the lighter fraction of invertase is accumulating during the first stage of accumulation.

SUMMARY

1. The study of the variation of surface tension with time of invertase solutions has given indication of the possible presence of two types of molecules in invertase.

2. The accumulation is strongly dependent on pH. It appears that this substance becomes strongly hydrophilic at high pH.

3. Formalisation of invertase brings down accumulation perhaps due to polymerisation.

4. A method has been described for the calculation of the order of dimension of the accumulating invertase molecule from the spreading and accumulation data.

ACKNOWLEDGMENTS

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STUDIES IN THE CHEMICAL BEHAVIOUR OF SOME COMPOUNDS OF SULPHUR

Part I. Production of Disulphur Monoxide by the Combustion of Sulphur in Oxygen at Low Pressure

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(Communicated by Dr. B. Sanjiva Rao, F.A.SC.)

INTRODUCTION

IN 1933 Schenk[1] announced a new oxide of sulphur which he prepared by streaming sulphur dioxide at low pressure through a high voltage electric discharge. Presence of sulphur vapour radically increased the yield of the oxide. Attempts were made by Schenk and coworkers to prepare the oxide in a variety of ways.[2–5] In one of these methods[3] sulphur was burnt in oxygen under low pressure (5 mm. of Hg) in a " cold " luminiscent flame. The product was shown to possess strong absorption bands in the region 2,500–3,400 Å. By analysis of the product condensed in a liquid air trap, Schenk concluded that in this oxide the atomic ratio of sulphur to oxygen was unity.[6]

In 1929 Henri and Wolff[7] had obtained an emission band spectrum between 2,400 and 4,000 Å, on subjecting sulphur dioxide to a high-voltage condensed discharge, and had suggested that the spectrum was due to a new oxide of sulphur. This emission band was studied in detail by Martin[8] who suggested that the diatomic molecule functioning as emitter was sulphur monoxide (SO). Schenk assumed that the absorption band got by him and the emission band observed by Henri and Wolff, and by Martin, were both due to sulphur monoxide.

Cordes[9] however attributed the absorption band to diatomic sulphur molecule in meta-stable condition. Zeise[10] pointed out that the bands appeared whenever sulphur monoxide was formed, and at temperatures at which no appreciable quantity of elemental sulphur could be present as vapour.

Kondrat'eva and Kondrat'ev[11] critically examined the earlier work and concluded that the band spectrum in question was too complicated to be due to a diatomic molecule (of sulphur) but was probably due to S_2O_2. They

showed that the absorption spectrum obtained by Schenk did not correspond to the emission spectrum observed by Henri and Wolff, and by Martin.

Montgomery and Kassel[12] concluded from free energy calculations that the ' SO ' gas was in moderately stable equilibrium with sulphur and sulphur dioxide at flame temperatures but that it was unstable below 1,000° K. Golding[13] stated that only a very small equilibrium concentration of ' SO ' could be attained in a mixture of sulphur vapour and sulphur dioxide, even at 2,000° K.

The infra-red spectrum of ' sulphur monoxide ' prepared by the method of Schenk[1] was recently examined by Jones.[14] He also studied the ultra-violet absorption of the oxide. Jones concluded that the molecule of the lower oxide of sulphur could not be ' SO ' but was likely to be S_2O_2 as suggested by Kondrat'eva and Kondrat'ev.[11] It was however, felt by him that confirmatory evidence based on electron diffraction and microwave spectra was needed to settle the issue.

From the above, it may be concluded that the lower oxide of sulphur found in the above experiments is not sulphur monoxide (SO) but is probably its dimer S_2O_2.

The existence of a new lower oxide of sulphur—Disulphur monoxide—was reported by B. S. Rao.[15] He suggested that it was produced in solution in carbon tetrachloride by the reaction between sulphur monoxide and its dimer, formed when sulphur was burnt in oxygen at low pressure. The equation suggested was

$$SO + S_2O_2 \rightarrow S_2O + SO_2.$$

In view of the dispute about the existence of sulphur monoxide and the probability of the formation of disulphur monoxide during combustion of sulphur, it was considered necessary to study in detail the combustion in oxygen under reduced pressure.

Experimental

1. *Combustion of Sulphur.*—The apparatus used in the present work, for the combustion of sulphur, was essentially the same as described by Schenk.[3] It was however, found advantageous to burn the sulphur in a quartz tube (B. S. Rao[15]). Fig. 1 gives a diagrammatic sketch of the apparatus.

T_1 was a special stopcock for regulating the flow of dry oxygen at the desired pressure. Tube B attached to the quartz combustion Tube A (dia. 1″) was loosely plugged with glasswool that had been previously treated with acid, washed and carefully dried. This served to catch sulphur that was

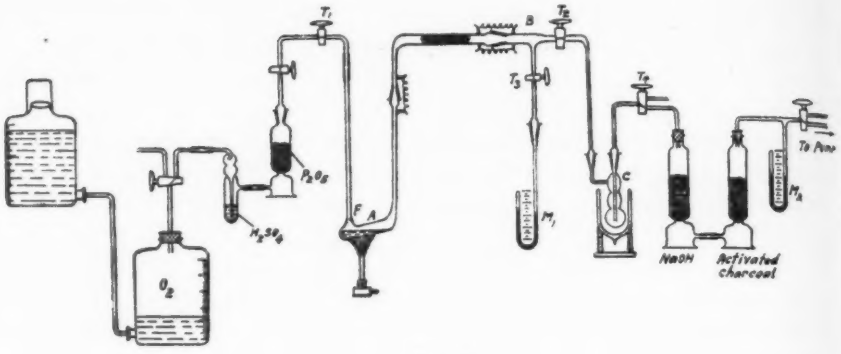

FIG. 1

carried by the gas stream. The receiver C (cooled in liquid air) was connected to the absorption towers through a three-way stopcock T_4. One of the absorption towers was packed with sodium hydroxide pellets and the other with activated charcoal. The special vacuum pump used, enabled the collection and measurement of the oxygen leaving T_4.

Tube A, containing about 75 g. of sulphur (A. R. Quality), was weighed before and after the combustion, to obtain the weight of sulphur consumed. A small correction had to be applied for elemental sulphur carried by the gas stream and deposited on the glass wool. A blank, in which nitrogen was passed over the heated sulphur, showed that the average weight of sulphur deposited on the glass wool was 4 mg.

Sulphur was melted under vacuum, and oxygen was let in at 5 to 7 mm. of Hg. A blue luminescent flame was noticed at F. An orange-red solid residue was formed in C. About 500 ml. of oxygen was used in each combustion. It was found that 85 to 90% of the oxygen passed, was consumed in the production of sulphur oxides.

Condenser C was disconnected and withdrawn, while still kept immersed in liquid air. It was however, noticed that if the liquid air bath was removed, and the orange red deposit allowed to warm up, the intensity of the colour of the deposit diminished markedly, though there was actually no decomposition of the lower oxide. The greater intensity of colour at low temperatures seemed to be due to polymerisation of the lower oxide molecule.

The orange-red residue was subjected to fractional evaporation in a stream of pure and dry hydrogen, C being kept at $-30°$ C. by a bath of alcohol cooled by carbon dioxide snow. Nitrogen was used in the earlier experiments. It was found however, that hydrogen was equally satisfactory.

The products of evaporation swept by hydrogen were absorbed in 2N sodium hydroxide containing glycerine (to minimise sulphite oxidation) and holding some cadmium hydroxide in suspension. It was found that at – 30° C., only sulphur dioxide was carried away by the hydrogen.

When the liberation of the sulphur dioxide was complete, the absorption vessels containing alkali were changed and the temperature of the bath raised to 25° C. It was noticed then that sulphur dioxide was freshly evolved at a slow rate. To complete the liberation of the gas, C was warmed to 60° C. (hot water-bath).

When the evolution of sulphur dioxide stopped completely, the sulphite formed in the absorption vessels was estimated iodometrically. C was weighed to determine the elemental sulphur deposited in it. In some experiments the sulphur deposited was estimated by the mercury sulphide method of B. S. Rao and M. R. A. Rao.[16] The experimental results are given in Table I.

As already stated, the orange-red deposit obtained at liquid air temperature, evolved sulphur dioxide when kept at — 30° C. This constituted the sulphur dioxide (Column '*c*', Table I) obtained as a primary product of combustion, and the gas liberated by the decomposition of disulphur dioxide in terms of equation (A)

$$3\,S_2O_2 \rightarrow 2\,S_2O + 2\,SO_2 \qquad \text{(A)}$$

$$2\,S_2O \rightarrow 3\,S + SO_2 \qquad \text{(B)}$$

On the complete removal of the sulphur dioxide, the deposit was warmed to 25° C. when there was fresh evolution of the dioxide and the liberation of sulphur. The ratio of elemental sulphur liberated, to the sulphur dioxide formed, was 3 (Column '*f*'). This showed that the oxide undergoing decomposition to liberate sulphur and sulphur dioxide was disulphur monoxide (Equation B). The evolution of sulphur dioxide at the second stage was slow and it was found necessary to warm the receiver to 60° C. to complete its liberation. This showed that the decomposition of disulphur monoxide was far less rapid than that of disulphur dioxide.

It can be seen from the above Equations A and B, that to evaluate sulphur corresponding to the disulphur dioxide decomposed, we have to add up the amount of elemental sulphur left over in C and 3 times the sulphur equivalent to that of sulphur dioxide obtained at the second stage. Values of sulphur corresponding to disulphur dioxide are given in Column '*h*'.

If it were practicable to directly determine the sulphur dioxide produced as primary product of combustion, the sulphur dioxide liberated by decomposition of S_2O_2, in terms of Equation A, could have been calculated from the

TABLE I

Products of Combustion of Sulphur in Oxygen under Reduced Pressure
(5 to 7 mm. of Hg.)

No. of expts.	*a* Oxygn consumed*	*b* Sulphur consumed*	*c* SO_2 liberated at −30° C.	*d* SO_2 liberated during heating to 60° C.	*e* Sulphur finally deposited in C.	*f* *e*/*d*	*g* *c*+*d*+*e* (Sulphur accounted)	*h* 3*d*+*e* (Lower oxide of sulphur formed)	*k* *h*/*a* × 100% yield of S_2O_3 on the basis of oxygen consumed
1	40·21	29·85	18·41	2·68	8·28	3·08	29·37	16·32	40·6
2	44·73	32·03	19·23	3·01	9·35	3·15	31·55	18·38	41·8
3	29·05	20·63	12·34	2·03	5·94	2·91	20·31	12·03	41·4
4	24·72	17·96	10·40	1·81	5·60	3·09	17·81	11·03	44·6
5	19·20	13·56	7·97	1·41	4·15	2·94	13·53	8·38	43·6
6	47·03	33·59	20·15	3·25	9·87	3·04	33·27	19·62	41·7
7	58·60	41·00	25·30	3·80	11·70	3·10	40·80	23·10	39·4
					Average ..	3·04			41·9

* Quantities of oxygen and sulphur are expressed in g. atoms × 10^3
and that of sulphur dioxide as corresponding to g. atoms of S × 10^3.

values in Column '*c*'. Unfortunately, sulphur dioxide primarily formed, cannot be determined.

In calculating sulphur corresponding to its lower oxides (Column '*h*'), it has been assumed that disulphur dioxide is the only lower oxide of sulphur formed as primary product. On this assumption, the amount of oxygen utilised in the production of the lower oxide of sulphur, is about 40% of the total oxygen consumed during combustion (Column '*k*'). Disulphur dioxide may not however, be the only lower oxide formed as primary product of combustion as it is likely that a certain amount of disulphur monoxide is also a primary product.

It was found by employing oxygen at various pressures that the yield of disulphur dioxide in these combustion experiments was dependent on the pressure of the oxygen. The following table (Table II) indicates the effect of pressure on the yield.

TABLE II

Effect of Pressure of Oxygen on the Yield of Lower Oxide of Sulphur

Range of oxygen pressure (in mm. of mercury)	1–2	3–4	5–7	9–12	15	25	35	45	50
Percentage yield of S_2O_2 ..	1 to 5	10 to 15	40 to 44	20 to 25	15	12	7 to 8	5	1 to 2

The optimum yield of disulphur dioxide (40–44%) was obtained at an oxygen pressure of 5–7 mm. of mercury.

2. *Effect of Temperature of Condensation on the Composition of the Deposit.*—The effect of temperature of condensation on the nature of the deposit formed in C, was then studied. Instead of using liquid air, a bath of alcohol cooled by carbon dioxide snow was employed for condensation. The products of combustion did not condense at − 50° C., but at − 65° C. to − 70° C., an orange-red deposit was obtained. It was noticed that the condensate scarcely held any sulphur dioxide. Continuing the stream of hydrogen (employed to sweep off any sulphur dioxide present), the temperature of the condensate was gradually raised to 60° C. and the sulphur dioxide liberated was absorbed in 2N alkali (holding cadmium hydroxide in suspension). Only a trace of cadmium sulphide could be detected. When the evolution of sulphur dioxide was complete, the sulphur compounds in the alkali absorbent were estimated. No thiosulphate was associated with the sulphite.

In another set of experiments, the decomposition of the lower oxides in the condensate was effected by shaking with mercury. The sulphur dioxide liberated, was absorbed in alkali and estimated. No cadmium sulphide could be detected in the alkali. The elemental sulphur present as residue in the receiver was determined by the mercury sulphid method. The results are tabulated below.

TABLE III

Decomposition of the Orange-Yellow Residue Obtained at — 70° C.

Thermal Decomposition (60° C.)				Decomposition with mercury			
Expt. No.	SO_2*	Elemental sulphur (S)	Ratio S to SO_2	Expt. No.	SO_2*	Elemental sulphur (S)	Ratio S to SO_2
1	8·18	25·12	3·09	1	3·86	12·05	3·12
2	5·64	17·05	3·03	2	9·12	28·26	3·10
3	15·48	48·15	3·11	3	12·46	39·54	3·17
4	12·85	39·56	3·08	4	7·58	23·86	3·14
5	21·25	62·95	2·96				
6	18·65	56·01	3·05				
		Average ..	3·05			Average ..	3·13

* Quantities of sulphur and its compounds are expressed in g. atoms of S $\times 10^4$.

The ratio obtained for elemental sulphur to sulphur dioxide (liberated when the orange-yellow deposit was decomposed) showed that the solid residue was practically disulphur monoxide.

As already indicated, a trace of cadmium sulphide was formed when the gas liberated by thermal decomposition was absorbed in alkali containing cadmium hydroxide suspension. The ratio of sulphur to sulphur dioxide was slightly lower in these experiments than in determinations wherein decomposition was effected with mercury. This showed that in the former series of decompositions, a little disulphur monoxide was carried away by the stream of hydrogen. It will be noticed that the ratio of sulphur to sulphur dioxide is a little higher than 3. This shows that even at — 70° C. there is a slight decomposition of disulphur monoxide to sulphur and sulphur dioxide. The sulphur dioxide escapes, but the sulphur remains behind in the condensate.

In another experiment, the products of combustion escaping condensation in receiver C at — 70° C., were bubbled through a strong solution of

potassium hydroxide cooled to − 5° C. Sulphide, sulphite and thiosulphate, present in the alkali absorbent, were determined, following the method of Kurtenacker and Goldbach.[17] From the sulphide and thiosulphate content of the absorbent solution, it could be concluded that quite an appreciable quantity of the disulphur dioxide formed during combustion escaped condensation in C at − 70° C.

This was confirmed by cooling the gas issuing from C in another receiver cooled by liquid air. An orange-red condensate was obtained. This was fractionally evaporated at − 30° C., till the evolution of sulphur dioxide ceased. The temperature was then slowly raised to 60° C. Sulphur dioxide freshly evolved at this stage as well as the residual sulphur (elemental) were determined. The analytical results showed that the ratio of elemental sulphur to sulphur dioxide was about 3·15. This confirmed that the disulphur dioxide was only partially condensed at − 70° C.

3. *Reaction between Alkali and the Products of Combustion.*—Certain experiments were then conducted to determine the nature of the orange-red deposit formed at − 70° C. in C. The deposit was treated with 2N caustic soda in which was suspended some cadmium hydroxide and the products of hydrolysis determined. The reaction products were sulphide, sulphite, thiosulphate and free sulphur. No sulphate or polythionate was formed. The elemental sulphur formed during the reaction was in the form of a precipitate mixed up with cadmium sulphide and hydroxide and was difficult to estimate accurately. The sulphur values have therefore, been omitted in the analytical results reported in Table IV.

TABLE IV

Reaction between Alkali and the Products of Combustion

Expt. No.	Sulphide*	Sulphite	Thiosulphate	$\frac{\text{Thiosulphate}}{\text{Sulphide}}$
1	19·25	21·64	73·72	3·83
2	6·45	7·25	25·36	3·94
3	8·16	9·05	32·56	3·99
4	14·72	15·78	58·10	3·95

* Quantities of sulphur compounds are expressed in terms of g. atoms of sulphur $\times 10^6$.

Schenk[1] reported that on treatment with alkali the condensate obtained by him gave, sulphide, sulphite and thiosulphate along with elemental sulphur but no sulphate, hydrosulphite or polythionates. It has to be mentioned

however, that Schenk and Cordes[18, 19] stated that in their earlier experiments sulphoxylate and hydrosulphite were formed. The formation of these oxy-salts could not be confirmed by later experiments (Schenk and Platz[4]). The present author has carried out a large number of experiments in which the products of combustion were treated with alkali. In no case has been obtained any sulphoxylate or hydrosulphite.

Schenk[2] suggested that thiosulphate was formed by the reaction between disulphur dioxide and alkali:

$$S_2O_2 + 2\ NaOH \rightarrow Na_2S_2O_3 + H_2O.$$

Sulphite was obviously due to sulphur dioxide present. The formation of sulphide and free sulphur however, was not accounted for by Schenk nor was any quantitative study made by him of the products formed.

It may be pointed out that the hydrolysis of sulphur monoxide or its dimer with alkali could yield sulphide, only if the reaction took place as follows:—

$$2\ SO \text{ or } S_2O_2 + 4\ NaOH \rightarrow Na_2S + Na_2SO_4 + 2\ H_2O.$$

Since no sulphate was formed along with the sulphide, the production of sulphide could not be due to the above reaction.

In the opinion of the present author, the sulphide was formed by the hydrolysis of disulphur monoxide present in the orange-red deposit:

$$S_2O + 4\ NaOH \rightarrow Na_2S + Na_2SO_3 + 2\ H_2O.$$

B. S. Rao[15] has shown that when a solution of disulphur monoxide in carbon tetrachloride is treated with alkali, sulphide, sulphite, thiosulphate and sulphur are produced as a result of three reactions that take place simultaneously:—hydrolysis, thionisation and decomposition. The relative magnitude of each reaction is affected by the dilution of the disulphur monoxide and by certain other factors.

The present author has also studied the reaction between alkali and carbon tetrachloride solutions of disulphur monoxide (Part III of present series). At moderate concentrations, 30% of the disulphur monoxide undergoes hydrolysis, 20% thionisation and the rest (50%) decomposition. It has to be pointed out that in the solutions studied by Rao,[15] free sulphur was present and this stabilised the oxide with the result decomposition was much less and hydrolysis correspondingly higher.

If it is assumed that the disulphur monoxide in the orange-red deposit undergoes the three simultaneous reactions on the percentage basis indicated above, it can be shown that the ratio of thiosulphate to sulphide formed when disulphur monoxide is treated with alkali will be about 2.

In Table V are given the relative ratios of thiosulphate to sulphide formed when (*a*) the products of combustion are absorbed in alkali directly on formation (Column A), (*b*) the orange-red deposit obtained on keeping at – 70° C. is treated with alkali (Column B), and (*c*) the orange-red deposit is kept for an hour more at – 70° C. and then allowed to react with alkali (Column C).

TABLE V

Expt. No.	Ratio Thiosulphate to sulphide		
	A Absorption of products of combustion by alkali, directly on formation	B Treatment of orange-red deposit with alkali	C Treatment of orange-red residue with alkali, one hour after formation
1	6·06	3·83	1·95
2	6·07	3·94	1·86
3	6·05	3·99	1·93
4	6·05	3·95	1·82
Average ..	6·06	3·90	1·90

It will be noticed that the ratio is nearly 2 in Column C, showing that on keeping the orange-red deposit for an hour, the lower oxide present in it is practically disulphur monoxide. On the other hand, the ratio in Column A is very much higher indicating the presence of disulphur dioxide. The ratios in Column B show that there has been a good deal of decomposition of disulphur dioxide, in the formation of the orange-red deposit. The decomposition of the dioxide gives the monoxide, as already indicated.

4. *Pressure Changes due to the Decomposition of the Gaseous Products of Combustion.*—As already indicated, the products of combustion of sulphur contain disulphur dioxide and disulphur monoxide along with sulphur dioxide. Oxygen would also be present in the gaseous mixture. For reasons discussed earlier, it is unlikely that any sulphur monoxide is present in the mixture.

When disulphur monoxide decomposes (Equation B) there is a 50% reduction in volume

$$2\,S_2O \rightarrow 3\,S + SO_2 \qquad \text{(B)}$$

The decomposition of disulphur dioxide probably takes place in two stages:—

$$3\,S_2O_2 \rightarrow 2\,S_2O + 2\,SO_2 \qquad (A)$$

$$2\,S_2O \rightarrow 3\,S + SO_2 \qquad (B)$$

$$3\,S_2O_2 \rightarrow 3\,S + 3\,SO_2$$

The final products however, are sulphur and sulphur dioxide. There is no change in volume on complete decomposition of the dioxide though at an intermediate stage there is an increase in volume corresponding to a third of the volume of the disulphur dioxide present.

Information regarding the presence of disulphur monoxide in the products of combustion can therefore, be obtained by following the pressure changes that arise on allowing decomposition to take place. The investigation was carried out in the following manner:

The products of combustion were collected in a 500 ml. flask fitted with suitable ground glass joints and stopcocks. The pressure of the gas inside the flask was measured with the help of a sulphuric acid manometer.[20] Neither mercury nor butyl phthalate could be used in the manometer because of their action on the lower oxides of sulphur. Even when sulphuric acid was used, there was a little error introduced due to solubility and decomposition effects. In reading the pressure, only momentary contact was made through a stopcock between the flask and the manometer. The decomposition of the lower oxides of sulphur was found to be complete in 4 to 6 hours at laboratory temperature (25° C.). By heating the flask in a water-bath at 95° C. the decomposition could be completed in less than 30 minutes.

A sample of the gaseous products collected in another 500 ml. flask, under the same conditions as above, was brought into contact with alkali which held some cadmium hydroxide in suspension. On completion of the reaction, the vacuum was released under nitrogen, and the resulting products analysed for sulphide, sulphite and thiosulphate in the usual way. The results are presented in Table VI.

The three simultaneous reactions which disulphur monoxide undergoes with alkali, have already been discussed. We may assume that the magnitude of the three reactions is the same when the disulphur monoxide is in the gaseous phase as when it is in the same concentration in carbon tetrachloride solution. If it is considered that 30% of the disulphur monoxide present undergoes hydrolysis, the disulphur monoxide content of the products of combustion can be calculated from the value of sulphide formed on treatment with alkali. This value is in agreement with that calculated on the basis of the pressure drop.

TABLE VI

Expt. No.	Initial pressure in cm. of H_2SO_4	Final fall in pressure in cm. of H_2SO_4	Sulphide*	Sulphite*	Thio-sulphate	S_2O calculated		S_2O_2 from the thio-sulphate values
						from pressure fall	from alkali reaction	
1	6·60	0·70	1·53	16·95	3·20	9·94	10·01	1·20
2	5·40	0·60	1·40	13·75	2·50	8·54	9·4	0·70
3	4·30	0·50	1·12	11·46	2·10	7·13	7·46	0·60
4	3·20	0·35	0·78	9·25	1·60	5·02	5·19	0·56
5	2·60	0·30	0·68	7·45	1·40	4·30	4·53	0·50
6	1·20	0·15	0·33	4·52	0·82	2·20	2·12	0·40

* Quantities of sulphur compounds are expressed in terms of g. atoms of S $\times 10^5$.

An approximate idea of the disulphur dioxide content of the gaseous system can be obtained from the observed thio-sulphate values after deducting the thiosulphate produced by disulphur monoxide (on the basis of 20% thionisation), it being assumed that (S_2O_2) quantitatively produces thiosulphate with alkali. Actually part of the (S_2O_2) may react with alkali to give sulphur and sulphite. The calculated disulphur dioxide values must therefore, be looked upon as minimum values for this oxide of sulphur, in the products of combustion.

When the pressure readings were taken at frequent intervals, it was noticed that in the initial stages (first half hour) of the decomposition of the products of combustion, there was a measurable increase in pressure, which was followed by a fall. This increase in pressure was of significance as it indicated the decomposition of (S_2O_2) to (S_2O) in terms of the equation given above.

At the stage at which there was no detectable pressure increase, there was, in general, a film of sulphur on the walls of the flask. On noticing this film, the gas in the flask was treated with alkali (containing cadmium hydroxide). It was found that very little thiosulphate was produced, while the sulphide content was appreciable. On similar treatment of the gas with alkali after a period of 4 hours (when the decomposition was usually complete) there was no sulphide or thiosulphate formed, and sulphite was the only product present.

It has already been mentioned in an earlier part of this paper that the spectroscopic data on the lower oxide of sulphur formed when sulphur is

burnt in oxygen under low pressure or when a condensed discharge is passed through a mixture of sulphur dioxide and sulphur vapour, show that the molecule of the oxide concerned is not diatomic. 'SO' is thus ruled out and the alternatives left are S_2O and S_2O_2. The analysis of the spectrum of a polyatomic molecule presents many difficulties, as the multiplicity of the modes of vibration and rotation considerably complicates the interpretation of experimental data. A triatomic molecule of the type (S_2O) will have only three fundamental frequencies ($3n-6$) and two of these have been observed in the infra-red spectrum by Jones. In the case of S_2O_2 on the other hand, there must be six fundamental frequencies. The spectroscopic evidence is thus in favour of the view that the oxide giving the characteristic absorption bands is disulphur monoxide. The observed PR structure of 15–18 cm.$^{-1}$ does not contradict this conclusion. Chemical evidence supporting the presence of disulphur monoxide has already been discussed.

Experimental evidence obtained by the present author indicated that disulphur monoxide is formed by the decomposition of disulphur dioxide. B. S. Rao[15] suggested that disulphur monoxide was formed by the reaction between S_2O_2 and SO.

As there is no spectroscopic evidence for the presence of "SO" in the products of combustion, it has to be assumed that the "SO" required for the above reaction is produced by the dissociation of S_2O_2 and that the SO, immediately on formation, reacts with (S_2O_2) to give (S_2O) and sulphur dioxide. While there is ample evidence that disulphur monoxide is produced by the decomposition of disulphur dioxide, the possibility of disulphur monoxide being also a primary product of the combustion of sulphur cannot be ruled out.

SUMMARY

1. A detailed study has been made of the combustion of sulphur in oxygen under low pressure when the lower oxides of sulphur, principally disulphur dioxide is produced. The best yield of the lower oxides is obtained at an optimum pressure of oxygen corresponding to 5 to 7 mm. of mercury.

2. When the products of combustion of sulphur are cooled under liquid air, an orange-red residue is obtained. This, when freed from sulphur dioxide at $-30°$ C., corresponds to S_2O. An orange-red deposit is also formed when the products of combustion are collected at $-70°$ C. At $-50°$ C. however, no deposit is got.

3. The orange-red deposit when treated with alkali, produces sulphide, sulphite and thiosulphate along with sulphur (no detectable amounts of

sulphate, hydrosulphite and polythionates are formed). A quantitative study of these products shows that they are formed by the action of alkali on disulphur monoxide (S_2O).

4. When the products of combustion are collected in a suitable vessel and decomposed, there is at first a slight rise and then a fall in pressure. The significance of the observed pressure changes is discussed. The increase in pressure is due to the decomposition of disulphur dioxide to disulphur monoxide while the fall in pressure is caused by the further decomposition of disulphur monoxide into sulphur and sulphur dioxide.

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QUASI-MONOTONE SERIES AND AN EXTENSION OF DVORETZKY'S THEOREM

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Dvoretzky [1, 167–69] has proved that if Σc_n be a monotone convergent series of positive terms and Σd_n be a monotone divergent series of positive terms then, for every $k > 1$, there exist infinitely many R_i, $R_i \to \infty$, such that for all n with $R_i \leqslant n \leqslant kR_i$, we have $c_n < d_n$. Szasz [2, 203–204] proved that this result holds if the two series $\Sigma c_n < \infty$, $\Sigma d_n = \infty$ be quasi-monotone. In this note we show that this result holds even if the series Σc_n be divergent but less rapidly divergent than Σd_n.

Theorem.—*Let Σu_n and Σd_n be two series such that for some constant $\alpha \geqslant 0$,*

$$0 < u_{n+1} \leqslant u_n\left(1 + \frac{\alpha}{n}\right),\ 0 < d_{n+1} \leqslant d_n\left(1 + \frac{\alpha}{n}\right) \tag{1}$$

for all $n > n_0(\alpha)$,

$$\Sigma d_n = \infty \tag{2}$$

$$\limsup_{n\to\infty} \frac{u_1 + u_2 + \ldots + u_n}{d_1 + d_2 + \ldots + d_n} = a < 1, \tag{3}$$

and let $0 \leqslant a < c < 1$, $k = \left(\frac{1}{c}\right)^{1/(3\alpha+2)}$. Then there exist infinitely many R_i, $R_i \to \infty$, such that for all n with $R_i \leqslant n \leqslant kR_i$ we have $u_n < d_n$.

Corollary.—Let Σu_n and Σd_n satisfy conditions (1) *and* (2), *and let*

$$\lim_{n\to\infty} \frac{u_1 + u_2 + \ldots + u_n}{d_1 + d_2 + \ldots + d_n} = 0 \tag{4}$$

Then for every $k > 1$, there exist infinitely many R_i, $R_i \to \infty$ such that for all n with $R_i \leqslant n \leqslant kR_i$ we have $u_n < d_n$.

2. *Proof of Theorem.*—Let $b = (a + c)/2$ and N $(> n_0)$ be so large that $k^N - k^{N-1} \geqslant 2$. Put

$$U_n = \sum_{[k^{n-1}]}^{[k^n]-1} u_\nu, \quad D_n = \sum_{[k^{n-1}]}^{[k^n]-1} d_\nu.$$

Let $u_\nu \geqslant d_\nu$ for some ν in the range $k^{n-1} \leqslant \nu \leqslant k^n$ $(n > N)$. Consider first when $[k^{n-1}] + 1 \leqslant \nu \leqslant [k^n] - 2$. We write sometime $u(p)$ for u_p and obtain from (1)

$$u_\nu \leqslant u([k^{n-1}]) \left(1 + \frac{a}{[k^{n-1}]}\right) \ldots \left(1 + \frac{a}{\nu - 1}\right)$$

$$= u([k^{n-1}])\, \Pi_1 \text{ say,}$$

$$d([k^n] - 1) \leqslant d_\nu \left(1 + \frac{a}{\nu}\right) \ldots \left(1 + \frac{a}{[k^n] - 2}\right)$$

$$= d_\nu\, \Pi_2 \text{ say,}$$

$$u([k^{n-1}])\, \Pi_1 \geqslant u_\nu \geqslant d_\nu \geqslant d([k^n] - 1)/\Pi_2. \tag{5}$$

Let p and q be any integers such that $[k^{n-2}] \leqslant p \leqslant [k^{n-1}] - 1$, $[k^n] \leqslant q \leqslant [k^{n+1}] - 1$. Then from (5) we get

$$u_p \geqslant d_q/\Pi \tag{6}$$

where

$$\Pi = \exp\left\{\sum_{t=[k^{n-2}]}^{[k^{n+1}]-1} \log\left(1 + \frac{a}{t}\right)\right\}.$$

It is easily seen that (6) holds when $\nu = [k^{n-1}]$ or $[k^n] - 1$ or $[k^n]$. Further for all $n > N_1$ $(> N)$

$$\Pi < \exp\left\{a \sum_{[k^{n-2}]}^{[k^{n+1}]-1} \frac{1}{t}\right\} < k^{3a} \left(\frac{c}{b}\right)^{\frac{1}{2}} = B \text{ (say).}$$

Hence

$$u_p > d_q/B,$$

$$\frac{U_{n-1}}{[k^{n-1}] - [k^{n-2}]} > \frac{1}{B} \frac{D_{n+1}}{[k^{n+1}] - [k^n]}$$

and so for $n > N_2$ $(> N_1)$

$$U_{n-1} > \frac{1}{Bk^2} \left(\frac{b}{c}\right)^{\frac{1}{2}} D_{n+1}.$$

If this relation holds for all large n, say $n \geqslant M\ (> N_2)$ then for $p > M$

$$\sum_{1}^{[k^{p+1}-1]} u_\nu > \frac{1}{Bk^{\frac{1}{2}}}\left(\frac{b}{c}\right)^{\frac{1}{2}} \sum_{[kM]}^{[k^{p+1}-1]} d_\nu.$$

Hence for $p > p_0\ (> M)$

$$\sum_{1}^{[k^{p+1}]-1} u_\nu > \frac{1}{Bk^{\frac{1}{2}}}\left(\frac{b}{c}\right)^{\frac{1}{2}} \sum_{1}^{[k^{p+1}]-1} d_\nu = c\left(\frac{b}{c}\right)^{3.4} \sum_{1}^{[k^{p+1}]-1} d_\nu$$

which contradicts (3). Hence the theorem is proved. The corollary follows immediately from the theorem.

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A NEW SYNTHESIS OF THIOPHENES AND THIAPYRANS

Part VII. Bromothionaphthenes and 5-Nitrothionaphthene

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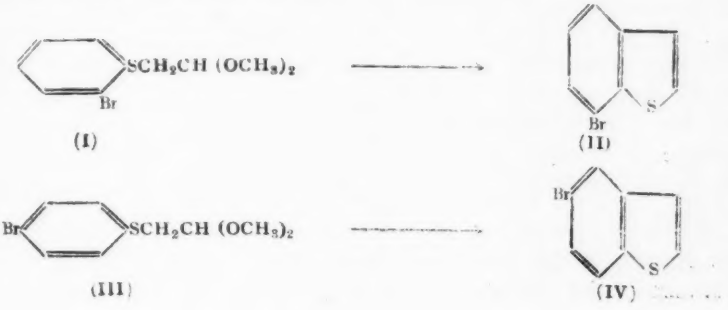
The synthesis of 5-chloro, 6-chloro, and 7-chlorothionaphthenes have been described by us recently.[1] Of the other monohalogenothionaphthenes, only the 3-bromo derivative has been reported in the literature.[2] We have recently described briefly the synthesis of 7-bromothionaphthene[3] (II). This compound is now fully described in addition to the hitherto unreported 5-bromothionaphthene (IV).

o-Bromothiophenol was condensed with bromoacetaldehyde dimethyl acetal to give *o*-bromophenyl ω- dimethoxyethyl sulphide (I). Cyclization of (I) with a mixture of phosphorus pentoxide and phosphoric acid gave (II) in 75% yield.

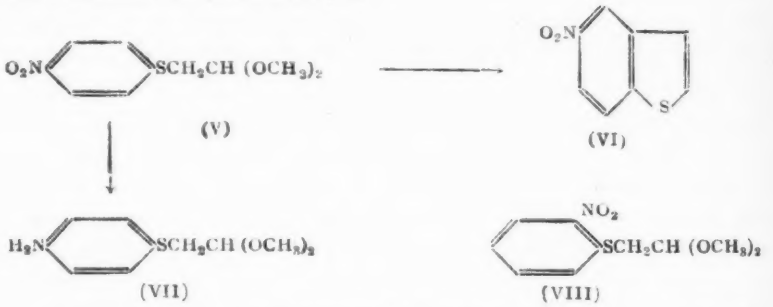
p-Bromothiophenol was condensed with bromoacetaldehyde dimethyl acetal to give *p*-bromophenyl ω-dimethoxyethyl sulphide (III). When (III) was cyclized with phosphorus pentoxide and phosphoric acid in the usual way, most of the sulphide (III) distilled over unchanged along with a very small quantity of the thionaphthene (IV). The quantities of phosphorus pentoxide and phosphoric acid were then doubled, and the sulphide added to the phosphorus pentoxide-phosphoric acid mixture kept at 130–40°/10 mm. The sulphide (III) does not distil under these conditions, whereas the thionaphthene (IV) distills over. The crude thionaphthene was purified by steam distillation (yield 13%).



(I) (II) (III) (IV)

Syntheses of substituted thionaphthenes by the cyclization of ary ω-dimethoxyethyl sulphides where the aryl group is phenyl in which *o*-, *p*-directing groups such as methyl, methoxy, ethoxy, chlorine or bromine are present, have been described in the present and previous communications.[4] It was of interest to synthesize nitrothionaphthenes by the ring-closure of nitrophenyl ω-dimethoxyethyl sulphides, although the cyclization of the latter was likely to prove difficult.

Of the six possible mononitrothionaphthenes, 3-, 4- and 5-nitrothionaphthenes are known. 3-Nitrothionaphthene[5] is obtainable by direct nitration of thionaphthene in acetic acid. Nitration with potassium nitrate in sulphuric acid leads to a mixture of dinitro and trinitrothionaphthenes from which the 3 : 4-dinitroderivative is separated by crystallization. A solution of the latter in alcoholic ammonia on treatment with hydrogen sulphide gives 4-nitrothionaphthene,[6] although the method does not appear to be unambiguous. 5-Nitrothionaphthene[7] is obtained synthetically starting from 2-chloro-5-nitrobenzaldehyde.



p-Nitrophenyl ω-dimethoxyethyl sulphide (V) was prepared by the condensation of bromoacetaldehyde dimethyl acetal with *p*-nitrothiophenol. Cyclization of (V) proved to be difficult in the initial experiments but success was achieved by employing the special conditions given in the experimental part. Several attempts to effect the cyclization of (V) under milder conditions with phosphorus pentoxide and phosphoric acid and with sulphuric acid of different strengths in presence of glacial acetic acid proved unsuccessful. The nitrothionaphthene (VI) was characterized by reduction with hydrogen in presence of Raney nickel to the known 5-aminothionaphthene[6] and by the preparation of 5-acetaminothionaphthene from the latter.

Catalytic reduction of (V) with hydrogen in presence of Raney nickel gave *p*-aminophenyl ω-dimethoxyethyl sulphide (VII) which in preliminary experiments failed to cyclize by the usual method.

Condensation of *o*-nitrothiophenol with bromoacetaldehyde dimethyl acetal gave *o*-nitrophenyl ω-dimethoxyethyl sulphide (VIII) as an oil which partially decomposes during vacuum distillation. An analytical specimen of (VIII) could not therefore be prepared but it was characterized by preparation of 2:4-dinitrophenylhydrazone of the parent *S*-(*o*-nitrophenyl)thioglycolic-aldehyde. Ring-closure of (VIII) to 7-nitrothionaphthene by the usual method however proved unsuccessful, the only product isolated being 2:2′-dinitrodiphenyl disulphide.

Experimental

The condensation of bromothiophenols and nitrothiophenols with bromoacetaldehyde dimethyl acetal and the characterization of the resulting sulphides as 2:4-dinitrophenylhydrazones of the parent *S*-arylthioglycolic-aldehyde have been carried out according to the general method outlined earlier.[8]

O-Bromophenyl ω-dimethoxyethyl sulphide (*I*)

O-Bromothiophenol (14·2 g.), sodium (1·9 g.), bromoacetaldehyde dimethyl acetal (13 g.) and absolute alcohol (50 c.c.) were refluxed for 5 hours. The sulphide (19·6 g.) after distillation gave a colourless oil (16·2 g., yield 78%), b.p. 130–31° (bath temp.)/7 mm. (Found: C, 43·7; H, 4·7. $C_{10}H_{13}BrO_2S$ requires C, 43·3; H, 4·7%). 2:4-*Dinitrophenylhydrazone* gave fine orange-yellow needles from alcohol-ethyl acetate, m.p. 136° (Found: N, 13·1. $C_{14}H_{11}BrN_4O_4S$ requires N, 13·6%).

7-Bromothionaphthene (*II*)

The sulphide (I) (9·5 g.) was added to phosphorus pentoxide (38 g.) and phosphoric acid, sp. gr. 1·75 (23 c.c.) at 170–80°/10 mm. 7-Bromothionaphthene (5·45 g., yield 75%), which distilled over, on purification through the picrate, gave a colourless oil (2·8 g., yield 39%), b.p. 108–9° (bath temp.)/10 mm. (Found: C, 45·7; H, 2·5. C_8H_5BrS requires C, 45·0; H, 2·3%). The *picrate* crystallized in yellow needles from alcohol, m.p. 144–45° (Found: N, 9·9. $C_{14}H_8BrN_3O_7S$ requires N, 9·5%).

p-Bromophenyl ω-dimethoxyethyl sulphide (*III*)

p-Bromothiophenol (23·2 g.), sodium (3 g.), bromoacetaldehyde dimethyl acetal (22·7 g.) and absolute alcohol (100 c.c.) were refluxed for 4 hours. The crude sulphide (31 g.) on distillation gave a colourless oil (24·5 g., yield 72%), b.p. 142–44° (bath temp.)/10 mm. (Found: C, 43·1; H, 4·8. $C_{10}H_{13}BrO_2S$ requires C, 43·3; H, 4·7%). 2:4-*Dinitrophenylhydrazone* gave yellow needles from ethyl alcohol, m.p. 140–41° (Found: N, 13·6. $C_{14}H_{11}BrN_4O_4S$ requires N, 13·6%).

5-Bromothionaphthene (IV)

The sulphide (III) (5 g.) was gradually added to a mixture of phosphorus pentoxide (40 g.) and phosphoric acid (48 c.c.) at 130–40°/10 mm. The thionaphthene, which distilled over, was dissolved in ether and the ethereal solution shaken with aqueous sodium hydroxide to remove some *p*-bromothiophenol which was formed in the cyclization. After removal of ether, the residue was steam distilled. A yellow oil distilled over which soon solidified (0·5 g., yield 13%). On redistillation it gave a colourless oil, b.p. 105-7° (bath temp.)/10 mm., which solidified on cooling. The product gave colourless plates from alcohol, m.p. 47–47·5° (Found: C, 45·0; H, 2·6. C_8H_5BrS requires C, 45·0; H, 2·3%). The thionaphthene did not give a picrate.

p-Nitrophenyl ω-dimethoxyethyl sulphide (V)

p-Nitrothiophenol[9] (15·5 g.), prepared from *p*-nitrochlorobenzene, sodium (2·3 g.), bromoacetaldehyde dimethyl acetal (18 g.) and absolute alcohol (100 c.c.) were refluxed for 12 hours. After distillation of alcohol, the mixture was diluted with water and the sulphide which separated as a red orange precipitate was extracted with ether. The ether extract was washed with 10% caustic soda solution, then with water, dried over sodium sulphate and ether removed. The sulphide (16·5 g., 68%) was crystallized from benzene-*n*-hexane when it gave orange-yellow needles, m.p. 55° (Found: C, 49·2; H, 5·0; N, 6·2. $C_{10}H_{13}NO_4S$ requires C, 49·4; H, 5·3; N, 5·7%). 2:4-*Dinitrophenylhydrazone* crystallized from *n*-hexyl alcohol in orange needles, m.p. 185° (Found: N, 18·4; $C_{14}H_{11}N_5O_6S$ requires N, 18·6%).

5-Nitrothionaphthene (VI)

Phosphoric acid (25 c.c.) was added to a mixture of the sulphide (V) (5·5 g.) and phosphorus pentoxide (30 g.) and the mixture was immediately heated in an oil bath for 5 minutes at 130° and then added to crushed ice. Extraction of the mixture with benzene and removal of the solvent, gave the thionaphthene (2·5 g.) as an oil. It was redissolved in benzene and the solution was passed through a column of activated alumina. Removal of the solvent from the percolate gave a dark brown oil (1·2 g.), which after distillation and sublimation in vacuum gave needles (0·5 g.). Crystallization from benzene-*n*-hexane gave 5-nitrothionaphthene as pale yellow needles, m.p. 149° (Literature,[6] m.p. 150°) (Found: C, 53·6; H, 2·8. Calc. for $C_8H_5NO_2S$: C, 53·6; H, 2·7%).

5-Aminothionaphthene

A mixture of the thionaphthene (VI) (0·5 g.), Raney nickel (0·1 g.) and absolute alcohol (25 c.c.) was shaken in a Parr hydrogenator with

hydrogen for 8 hours at 42 lb./sq. inch. Removal of Raney nickel and evaporation of the alcoholic extract, gave 5-aminothionaphthene as a brown oil (0·4 g.), b.p. 145° (bath temp.) 2 mm. After crystallization from benzene-*n*-hexane, the thionaphthene gave, m.p. 70°. Acetylation of the amine gave 5-acetamidothionaphthene which crystallized from benzene-*n*-hexane in white flakes, m.p. 108°. M.p.s. quoted[6] for the amine and its N-acetyl derivative are 72° and 107° respectively.

p-Aminophenyl ω-dimethoxyethyl sulphide (VII)

A mixture of the sulphide (V) (2 g.), Raney nickel (0·1 g.) and absolute alcohol (30 c.c.) was shaken in a Parr hydrogenator with hydrogen for 6 hours at 42 lb./sq. inch. Removal of Raney nickel and evaporation of alcohol, gave *p*-aminophenyl ω-dimethoxyethyl sulphide, b.p. 200–5° (bath temp.)/25 mm. (1·58 g., yield 90%). After four redistillations it was finally collected at 185° (bath temp.)/4 mm. (Found: C, 56·3; H, 7·0; N, 6·7. $C_{10}H_{15}NO_2S$ requires C, 56·3; H, 6·8; N, 6·6%).

o-Nitrophenyl ω-dimethoxyethyl sulphide (VIII)

o-Nitrothiophenol (8 g.), prepared from *o*-nitrochlorobenzene,[10] sodium (1·2 g.), bromoacetaldehyde dimethyl acetal (9 g.) and absolute alcohol (50 c.c.) were boiled for 12 hours on water-bath. After removal of alcohol and dilution with water, a dark red oil was obtained, which was extracted with ether. Removal of ether gave a dark brown oil which on distillation gave yellow liquid, b.p. 140–80° (bath temp.)/4 mm. (yield, 6·0 g.). The sulphide does not give a sharp b.p. and partially decomposes during distillation. 2:4-*Dinitrophenylhydrazone* crystallized from hexyl alcohol in yellow needles, m.p. 180° (Found: C, 45·0; H, 3·3; N, 18·2. $C_{14}H_{11}N_5O_6S$ requires C, 44·6; H, 2·9; N, 18·6%).

Summary

5-Bromothionaphthene and 7-bromothionaphthene were prepared by the cyclization of *p*-bromophenyl ω-dimethoxyethyl sulphide and *o*-bromophenyl ω-dimethoxyethyl sulphide respectively.

The new synthesis of thionaphthene may also be extended to negatively substituted thionaphthenes as shown by the synthesis of 5-nitrothionaphthene (VI) by the ring-closure of *p*-nitrophenyl ω-dimethoxyethyl sulphide (V). *o*-Nitrophenyl ω-dimethoxyethyl sulphide could not be cyclized by the usual method. 5-Aminothionaphthene and *p*-aminophenyl ω-dimethoxyethyl sulphide were obtained by the reduction of (VI) and (V) respectively.

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THIOPHENES AND THIAPYRANS*

Part VIII. A New Synthesis of Dibenzothiophene and Its Derivatives; Its Scope and Limitations

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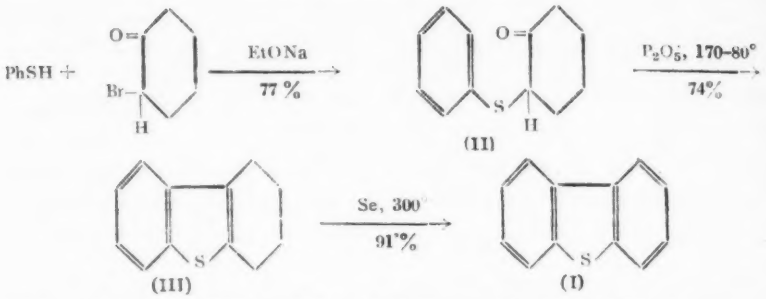
Dibenzothiophene (I) accompanies phenanthrene in the distillation of coal tar.[1] Attempts to prepare dyes[2] and physiologically active substances[3] from (I) have been reported. Several syntheses of (I) have been described in the literature,[4–7] but these are not very satisfactory, especially for substituted derivatives. A few 4-substituted derivatives of (I) have been prepared through metalation[6] and 2-substituted and 2:8-disubstituted derivatives are obtainable by direct substitution.[7–10] With the exception of these compounds other derivatives of (I) are not easily accessible.

Recently 3-methylthionaphthene and a number of 2:3-dimethylthionaphthenes and naphthothiophenes have been prepared by Werner[12] by the cyclization of α-arylmercaptoketones by treatment with phosphorus pentoxide or fused zinc chloride. The mercaptoketones were obtained by the condensation of aryl thiols with α-haloketones of the type; $R_1\text{–}\overset{x}{\underset{|}{C}}H\text{–}CO\text{–}R_2$, where x = halogen and R_1 and R_2 are alkyl groups. By the condensation of aryl thiols with α-halo cyclic ketones such as 2-bromocyclohexanone and ring-closure of the intermediate 2-arylmercaptocyclohexanones, it should be possible to fuse a tetrahydrothionaphthene ring system to the aromatic nucleus of the thiol. Dehydrogenation of the tetrahydro derivative would then lead to polycyclic derivatives containing a thionaphthene ring. This was in fact realized and dibenzothiophene (I) was prepared starting from thiophenol and 2-bromocyclohexanone by the following steps, the overall yield of pure (I) being 52%:

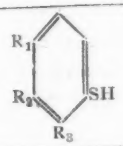
Dibenzofuran[13] and carbazole derivatives[14] have been prepared in a similar manner starting from phenols and aryl amines and 2-chlorocyclohexanone. A brief account of the above new synthesis of dibenzothiophene has been reported[15] upon recently by us, and the present paper gives the experimental details of the synthesis. The hitherto unreported 2-methyl-

* A general study of the synthesis of thiophenes and thiapyrans by different methods is projected and the title of the series has been modified accordingly.



dibenzothiophene (VI) and 3-methyldibenzothiophene (IX) have now been prepared by the above general method in addition to the known 4-methyldibenzothiophene[6] (XII) and 4-methoxydibenzothiophene[6] (XV). Synthesis of 2-methoxydibenzothiophene could not be completed on account of the low yields of 2-methoxy-6:7:8:9-tetrahydrodibenzothiophene (XVII) in the cyclization of 2-(4-methoxyphenylmercapto)cyclohexanone (XVI). Similar low yields have also been observed earlier in the cyclization of *p*-methoxyphenyl *ω*-dimethoxyethyl sulphide.[16] Attempts to synthesize 2-nitrodibenzothiophene were likewise unsuccessful. The condensation of *o*-methoxythiophenol and 2-bromocyclohexanone in ethanolic solution of sodium ethoxide gave a poor yield of 2-(2′-methoxyphenylmercapto)cyclohexanone (XIII). When the condensation was carried out in the presence of 35% aqueous sodium hydroxide[12] the yield of (XIII) was 77%. The synthesis of the dibenzothiophenes from the relevant thiophenols and the yield of the pure intermediates and final compounds in the synthesis have been summarized in Chart I.

CHART I

		2-Arylmercaptocyclohexanones		Tetrahydrodibenzothiophenes		Dibenzothiophenes
R_1=Me; R_2=R_3=H	—68%→	(IV)	—60%→	(V)	—46%→	(VI)
R_2=Me; R_1=R_3=H	—80%→	(VII)	—78%→	(VIII)	—79%→	(IX)
R_3=Me; R_1=R_2=H	—85%→	(X)	—62%→	(XI)	—57%→	(XII)
R_3=OMe; R_1=R_2=H	—77%→	(XIII)	—47%→	(XIV)	—33%→	(XV)
R_1=OMe; R_2=R_3=H	—75%→	(XVI)	→	(XVII)	Characterized as picrate	
R_1=NO_2; R_2=R_3=H	—93%→	(XVIII)				

The synthesis of dibenzothiophene and its derivatives described above demonstrates the general applicability of the new synthesis. The scope of the synthesis appears to be as wide as the synthesis of thiophenes and thiapyrans which have been described in previous communications.[17] Whereas in the latter synthesis a thiophene or a thiapyran ring is fused to an aromatic ring system of the aryl thiol, in the present synthesis, a thionaphthene ring is fused to the aryl nucleus of the thiol. The only requisites appear to be aryl thiols with free *o*- or peri-positions (in the case of naphthalene) to enable cyclization to take place.

The scope of the synthesis in the preparation of monosubstituted derivatives of dibenzothiophene appears to be limited to 2-, 3- and 4-substituted derivatives. Ortho- and para-substituted thiophenols lead to 4- and 2-substituted derivatives respectively. In the case of a *m*-substituted thiophenol, 1- or 3-substituted dibenzothiophene may result, depending on the direction of ring-closure of the intermediate 2-(3′-substituted-phenylmercapto) cyclohexanone. The cyclization of the latter however probably leads to a 3-substituted derivative in preference to a 1-substituted derivative on account of steric considerations. It has been noted earlier that in the analogous cyclization of 3-methylphenyl ω-dimethoxyethyl sulphide only 6-methylthionaphthene was formed (unpublished work). The cyclization product of (VII) is therefore constituted as 3-methyl-6 : 7 : 8 : 9-tetrahydrodibenzothiophene (VIII).

Starting from naphthalene monothiols and dithiols polycyclic compounds containing naphthalene and thionaphthene or benzothiapyran ring systems can be synthesized. Some of these compounds have already been prepared and will be reported upon in subsequent communications. Similarly starting with aryl thiols and substituted 2-bromocyclohexanones new substituted derivatives of (I) may be synthesized by the above method. By using suitably oriented bromotetralones in place of 2-bromocyclohexanone, other sulphur-containing polycyclic ring systems could also be synthesized.

One of the limitations of the synthesis at present is the drastic treatment involved in the cyclization of 2-arylmercapto-cyclohexanone with phosphorus pentoxide and in the subsequent selenium dehydrogenation of the tetrahydrodibenzothiophenes which may preclude its application to compounds which are unstable under these conditions. Experiments to carry out these steps under milder conditions are in progress.

EXPERIMENTAL

2-Phenylmercaptocyclohexanone (II)

Thiophenol (8·6 g.), sodium (2 g.), 2-bromocyclohexanone (15 g.) and alcohol (50 c.c.) were refluxed for 3 hours. The crude condensation product (16·5 g.) on distillation gave a colourless oil (12·8 g., yield 77%), b.p. 152–53° (bath temp.)/10 mm. (Found: C, 69·7; H, 6·5; $C_{12}H_{14}OS$ requires C, 69·9; H, 6·8%). The 2:4-*dinitrophenylhydrazone* gave lustrous yellow needles from alcohol-ethyl acetate, m.p. 162–3° (Found: C, 56·6; H, 5·1; N, 14·1. $C_{18}H_{18}N_4O_4S$ requires C, 56·0; H, 4·7; N, 14·5%).

1:2:3:4-Tetrahydrodibenzothiophene (III)

A mixture of (II) (7·4 g.) and phosphorus pentoxide (20 g.) was heated at 170–80° for 45 minutes. The product (6 g.) on distillation gave a colourless oil (5·01 g., yield, 74%), b.p. 141° (bath temp.)/10 mm. (Found: C, 76·6; H, 6·5. Calc. for $C_{12}H_{12}S$: C, 76·6; H, 6·4%). The compound has been reported upon earlier being prepared by Clemmensen reduction of 1-keto-1:2:3:4-tetrahydrodibenzothiophene.[18] The *picrate* gave orange needles from alcohol, m.p. 108–09° (Found: N, 9·6. $C_{18}H_{15}N_3O_7S$ requires N, 10·1%).

Dibenzothiophene (I)

Tetrahydrodibenzothiophene (III) (1·5 g.) and selenium (1·4 g.) were heated at 300° for 22 hours. Extraction of the mixture with alcohol gave a crystalline product (1·33 g., yield 91%) which on crystallization from alcohol gave long colourless needles, m.p. 98°, of dibenzothiophene (literature[6, 18] m.p., 95–6° and 99°) (Found: C, 77·8; H, 4·5. Calc. for $C_{12}H_8S$: C, 78·3; H, 4·4%). The *picrate* gave yellow needles from alcohol, m.p. 123–4° (Gilmann and Jacoby,[6] 125°) (Found: N, 10·3. Calc. for $C_{18}H_{14}N_3O_7S$: N, 10·2%).

2-(4'-Methylphenylmercapto)cyclohexanone (IV)

p-Thiocresol (9 g.), sodium (1·8 g.), 2-bromocyclohexanone (13·5 g.) and alcohol (50 c.c.) were refluxed for 5 hours. The condensation product (12·5 g.) on distillation gave a straw coloured oil (10·8 g., yield 68%), b.p., 168–73° (bath temp.)/5 mm. (Found: C, 70·8; H, 7·2. $C_{13}H_{16}OS$ requires C, 70·9; H, 7·3%). The 2:4-*dinitrophenylhydrazone* gave orange needles from alcohol-ethyl acetate, m.p. 161–2° (Found: N, 14·6. $C_{19}H_{20}N_4O_4S$ requires N, 14·0%).

2-Methyl-6:7:8:9-tetrahydrodibenzothiophene (*V*)

A mixture of (IV) (6·1 g.) and phosphorus pentoxide (18 g.) was heated at 175–80° for 30 minutes. The cyclization product which was a brown oil (4·6 g.) on distillation gave a colourless liquid (3·38 g., yield 60%), b.p. 165–70° (bath temp.)/5 mm. (Found: C, 77·2; H, 7·5. $C_{13}H_{14}S$ requires C, 77·2; H, 6·9%). The *picrate* gave orange red needles from alcohol, m.p. 112–3° (Found: N, 9·5. $C_{19}H_{17}N_3O_7S$ requires N, 9·7%).

2-Methyldibenzothiophene (*VI*)

A mixture of (V) (2·07 g.) and selenium (1·9 g.) was heated at 300° for 16 hours. The mixture on extraction with alcohol gave cream coloured crystals (0·93 g., yield 46%), m.p. 80–3°. After two crystallizations from alcohol the thiophene (VI) gave colourless needles, m.p. 85·5° (Found: C, 78·6; H, 5·1. $C_{13}H_{10}S$ requires C, 78·8; H, 5·1%). The *picrate* gave curved orange needles from alcohol, m.p. 117–8° (Found: N, 9·7. $C_{19}H_{13}N_3O_7S$ requires N, 9·8%).

2-(3'-Methylphenylmercapto)cyclohexanone (*VII*)

m-Thiocresol (10·1 g.), sodium (2 g.), 2-bromocyclohexanone (15·4 g.) and alcohol (50 c.c.) were refluxed for 6 hours. The condensation product (16·5 g.) on distillation gave a colourless oil (14·4 g., yield 80%), b.p. 168–70° (bath temp.)/11 mm. (Found: C, 70·4; H, 7·5. $C_{13}H_{16}OS$ requires C, 70·9; H, 7·3%). The 2:4-*dinitrophenylhydrazone* gave yellow needles from alcohol-ethyl acetate, m.p. 146–7° (Found: N, 13·9. $C_{19}H_{20}N_4O_4S$ requires N, 14·0%).

3-Methyl-6:7:8:9-tetrahydrodibenzothiophene (*VIII*)

A mixture of (VII) (4·2 g.) and phosphorus pentoxide (12 g.) was heated at 170–80° for 45 minutes. The thiophene (VIII; 3·1 g.) on distillation gave a colourless liquid (3·02 g., yield 78%), b.p. 137–9° (bath temp.)/9 mm. (Found: C, 76·9; H, 7·0. $C_{13}H_{14}S$ requires C, 77·2; H, 6·9%). The *picrate* crystallized from alcohol in orange-red needles, m.p. 88–9° (Found: N, 9·4. $C_{19}H_{17}N_3O_7S$ requires N, 9·7%).

3-Methyldibenzothiophene (*IX*)

The above thiophene (VIII) (1·57 g.) and selenium (1·36 g.) were heated at 300° for 22 hours. The crude product (1·22 g.) isolated by extraction with alcohol on distillation gave a colourless oil (1·15 g., yield 79%), b.p. 175–80° (bath temp.)/10 mm. (Found: C, 78·5; H, 5·4. $C_{13}H_{10}S$ requires C, 77·8; H, 5·1%). The *picrate* gave yellow needles from alcohol, m.p. 97° (Found: N, 9·8. $C_{19}H_{13}N_3O_7S$ requires N, 9·8%).

2-(2′-*Methylphenylmercapto*)*cyclohexanone*

o-Thiocresol (10·7 g.), sodium (2·1 g.), 2-bromocyclohexanone (16 g.) and alcohol (50 c.c.) were refluxed for 7 hours. The condensation product (18·3 g.) on distillation gave a pale yellow oil (15·6 g., yield 85%), b.p. 165–70° (bath temp.)/8 mm. (Found: C, 71·3; H, 7·6. $C_{13}H_{16}OS$ requires C, 70·9; H, 7·3%). The 2:4-*dinitrophenylhydrazone* gave orange yellow needles from alcohol-ethyl acetate, m.p. 143–44° (Found: N, 13·9. $C_{19}H_{20}N_4O_4S$ requires N, 14·0%).

4-*Methyl*-6:7:8:9-*tetrahydrodibenzothiophene* (*XI*)

A mixture of (X) (7·8 g.) and phosphorus pentoxide (24 g.) was heated at 165–70° for 45 minutes. The cyclization product (5·7 g.) on distillation gave a pale yellow oil (4·39 g., yield 62%), b.p. 145–50° (bath temp.)/6 mm. (Found: C, 77·3; H, 7·2. $C_{13}H_{14}S$ requires C, 77·2; H, 6·9%). The *picrate* gave orange yellow needles from alcohol, m.p. 95–6° (Found: N, 9·9. $C_{19}H_{17}N_3O_7S$ requires N, 9·7%).

4-*Methyldibenzothiophene* (*XII*)

A mixture of (XI) (2·99 g.) and selenium (2·7 g.) was heated at 300° for 22 hours. The crude product isolated by means of alcohol was a brown liquid (2·56 g.) which solidified on cooling and showed green fluorescence. On distillation it gave a pale yellow liquid, b.p. 100–04° (bath temp.)/5 mm. which partly solidified. The product was therefore purified through the picrate which was decomposed with 1% aqueous ammonia. The colourless crystals of the purified thiophene (XII) (1·4 g., yield 51%), m.p. 59–61° after two crystallizations from alcohol gave lustrous, colourless plates, m.p. 66·5° (Found: C, 78·6; H, 5·1. Calc. for $C_{13}H_{10}S$: C, 78·8; H, 5·1%). The *picrate* gave lemon yellow needles from alcohol, m.p. 110° (Found: N, 9·7. $C_{19}H_{13}N_3O_7S$ requires N, 9·8%).

2-(2′-*Methoxyphenylmercapto*)*cyclohexanone* (*XIII*)

o-Methoxythiophenol (10·2 g.) was dissolved in 35% aqueous sodium hydroxide (8·35 c.c., 1 mol.). After cooling the solution to 20–25°, 2-bromocyclohexanone (13·5 g., 1 mol.) was added dropwise in 15 minutes under stirring and cooling. After stirring for one hour, the contents were diluted with water and extracted with ether. The product (17·7 g.) on distillation gave a colourless oil (13·2 g., yield 77%), b.p. 190–5° (bath temp.)/5 mm. (Found: C, 65·4; H. 6·5. $C_{13}H_{16}O_2S$ requires C, 66·1; H, 6·8%). The 2:4-*dinitrophenylhydrazone* gave orange needles from alcohol, m.p. 130–1° (Found: N, 13·5. $C_{19}H_{20}N_4O_5S$ requires N, 13·5%).

4-Methoxy-6 : 7 : 8 : 9-tetrahydrodibenzothiophene (XIV)

A mixture of (XIII) (2·7 g.) and phosphorus pentoxide (9 g.) was heated at 170–80° for 30 minutes. The product, a thick dark oil (1·8 g.), gave on distillation a yellow oil (1·2 g., yield 47%), b.p. 180–200° (bath temp.)/5 mm., which soon solidified. On crystallization from alcohol, the thiophene (XIV) gave colourless needles, m.p. 83·5° (Found: C, 71·1; H, 6·4. $C_{13}H_{14}OS$ requires C, 71·5; H, 6·4%). The *picrate* gave orange-red needles from alcohol, m.p. 134–5° (Found: N, 9·5. $C_{19}H_{17}N_3O_8S$ requires N, 9·4%).

4-Methoxydibenzothiophene (XV)

A mixture of (XIV) and selenium (1·35 g.) was heated at 300° for 16 hours. The crystals (0·5 g.) isolated by extraction with alcohol gave on sublimation at 130–5°/5 mm. colourless needles (0·45 g., yield 30%), m.p. 122°; unaltered by crystallization from alcohol (Gilman and Jacoby[6] quote m.p. 123°) (Found: C, 73·1; H, 4·8. Calc. for $C_{13}H_{10}OS$: C, 72·9; H, 4·7%). The *picrate* gave orange-red needles from alcohol, m.p. 118° (Found: N, 9·3. $C_{19}H_{13}N_3O_8S$ requires N, 9·5%).

2-(4'-Methoxyphenylmercapto)cyclohexanone (XVI)

p-Methoxythiophenol (9 g.), sodium (1·6 g.), 2-bromocyclohexanone (12·4 g.) and alcohol (50 c.c.) were refluxed for 6 hours. The product (15·2 g.) on distillation gave a straw-coloured oil (11·8 g., yield 75%), b.p. 175–80° (bath temp.)/5 mm. (Found: C, 65·3; H, 6·8. $C_{13}H_{16}O_2S$ requires C, 66·1; H, 6·8%). The 2 : 4-*dinitrophenylhydrazone* gave orange red needles from alcohol-ethyl acetate, m.p. 120–1° (Found: N, 14·1. $C_{19}H_{20}N_4O_5S$ requires N, 13·5%).

2-Methoxy-6 : 7 : 8 : 9-tetrahydrodibenzothiophene (XVII)

A mixture of (XVI) (3·64 g.) and phosphorus pentoxide (11 g.) was heated at 170–5° for 30 minutes. The cyclization product (1·65 g.) on distillation gave a fraction (0·14 g.), b.p. 175–80° (bath temp.)/5 mm. which gave a *picrate*. Lower boiling fraction mainly consisted of the parent thiol. The above fraction was converted into the *picrate* which on two crystallizations from alcohol gave orange red needles, m.p. 120–1° (Found: C, 52·6; H, 4·3; N, 8·8. $C_{19}H_{17}O_8N_3S$ requires C, 51·0; H, 3·8; N, 9·4%).

2-(4'-Nitrophenylmercapto)cyclohexanone (XVIII)

A solution of *p*-nitrothiophenol (8 g.) in 35% aqueous sodium hydroxide (5·9 c.c., 1 mol.) was cooled to 20–25° and 2-bromocyclohexanone (9·5 g.) was gradually added in 10 minutes under stirring and cooling. After stirring for 1½ hours the reaction mixture was diluted with water and the product

which separated was collected (12 g., yield 92%) and crystallized from benzene-petroleum ether. It gave minute needles, m.p. 93–4° (Found: C, 56·6; H, 4·8; N, 5·4. $C_{12}H_{13}O_3NS$ requires C, 57·4; H, 5·2; N, 5·6%). The 2:4-*dinitrophenylhydrazone* gave orange plates from alcohol, m.p. 167–8° (Found: N, 15·8. $C_{18}H_{17}N_5O_6S$ requires N, 16·2%).

SUMMARY

A new synthesis of dibenzothiophene (I) which has been extended to its substituted derivatives has been developed. It consists in the condensation of thiophenol with 2-bromocyclohexanone to give 2-phenylmercaptocyclohexanone (II), cyclization of (II) with phosphorus pentoxide to 1:2:3:4-tetrahydrodibenzothiophene and selenium dehydrogenation of the latter compound to give (I) (overall yield 52%).

Starting with suitably substituted thiophenols, 2-methyl-, 3-methyl and 4-methyldibenzothiophenes and 4-methoxydibenzothiophene have been synthesized. The synthesis of 2-methoxydibenzothiophene could not be completed due to the low yield of 2-methoxy-6:7:8:9-tetrahydrodibenzothiophene. Attempts to cyclize 2-(4′-nitrophenylmercapto)cyclohexanone by means of phosphorus pentoxide by the usual method were unsuccessful.

The scope and limitations of the new synthesis are discussed.

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ERRATA

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Page 302: The names of the fusaria for Figs. 1 and 2, please read as follows:

Fig. 1. *Fusarium vasinfectum.*

Fig. 2. *Fusarium moniliforme.*